

GENERAL CHEMISTRY

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The two royal physicians were not a
father and son.

GENERAL CHEMISTRY

HARRY N. HOLMES OF BERLIN COLLEGE

FIFTH EDITION

THE MACMILLAN COMPANY · NEW YORK

Fifth Edition

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PREFACE

The fifth edition of this text keeps pace with the rapid changes in theory, and their application to industry, that have taken place since the appearance of the previous edition. The concepts of electrovalence, covalence, and coordinate covalence are freely used, as is the theory of practically complete ionization of salts and the strongest acids and bases. The discussion of the structure of the atom is introduced very early and repeated frequently. Relative sizes of ions in crystals are given attention.

Nuclear chemistry, with the modern development of uranium fission and atomic energy, is given extended treatment. The improved long form of the Table of Atomic Numbers introducing the newest elements in an actinide series is an added feature. The Brönsted theory of acids and bases is developed in a separate chapter with the application optional.

The metals are classified according to methods of preparation rather than by the common tiresome encyclopedic arrangement. However, compounds of the metals, their properties and uses, are arranged approximately in accordance with their periodic grouping. The growing practice of bringing qualitative analysis into the second semester of the first year course is greatly aided by earlier introduction of compounds of the metals.

Industrial applications are brought up to date with special emphasis on synthetic rubber, the synthetic fibers, plastics, petroleum chemistry and the newer synthetic drugs. New teaching aids such as charts and tables are used freely. An extended form of the activity series of metals is introduced.

In general the aim of this text is to lay an adequate foundation for advanced chemistry while training citizens in appreciation and understanding of scientific thinking.

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H. N. H.

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GENERAL CHEMISTRY



Purdue University placed this bas relief above the entrance to their School of Chemistry and Metallurgical Engineering. Symbolistic are the blast furnace, filter press, autoclave, acid tank car and the crossed alembics of alchemy.

Chapter I BASIC PRINCIPLES

This Chemical Age. Every member of this class enjoys the benefits of chemistry. His means of transportation to college — by auto, train or plane — was connected with the chemical preparation of strong materials and excellent fuels. His clothing was chemically bleached or dyed, perhaps made of synthetic fibers and the books under his arm were made of chemically treated paper, prepared inks, and glue.

If he desires relaxation from exhausting study, the student may enjoy the results of the chemist's skill in producing transparent flexible movie film coated with sensitive silver bromide, that is chemically changed by light into an interesting pattern of pictures.

Our civilization rests upon chemical foundations. When primitive man first employed fire as a tool, he accentuated the differences between man and the other animals. And fire is the chemical tool which made possible the Bronze Age, the Iron Age, and the Age of Machinery.

Think of surgery without anesthetics and antiseptics; of airships without light, strong alloys, and without gas or gasoline; of clothing without dyes; painting without colored pigments. We might almost as well try to build bridges and office buildings without steel and concrete; to dig tunnels and a Panama Canal without explosives.

The greatest advances in medicine are now chemical, where once they were biological. Our attack upon disease by beneficent

drugs is chemical. So is the digestion of food. So are the most vital processes of animal and plant growth.

The dollar measure of chemical industries shows the great importance of

Petroleum	Drugs and Medicines	Rayon, Nylon
Leather	Manufactured Gas	Lime
Paper	Brick and Clay Products	Cement
Rubber	Coal By-products	Paints
Sugar	Fertilizers	Fats
Glass	Explosives	Soaps
Plastics	Cosmetics	Dyes

What Is Chemistry? *Chemistry treats of the composition and changes in composition of substances. It is also concerned with their properties and their energy relations. Like all the other sciences chemistry classifies observed facts for use.*

We may go further and state that chemistry deals with the detection of substances, their separation from mixtures, and their preparation.

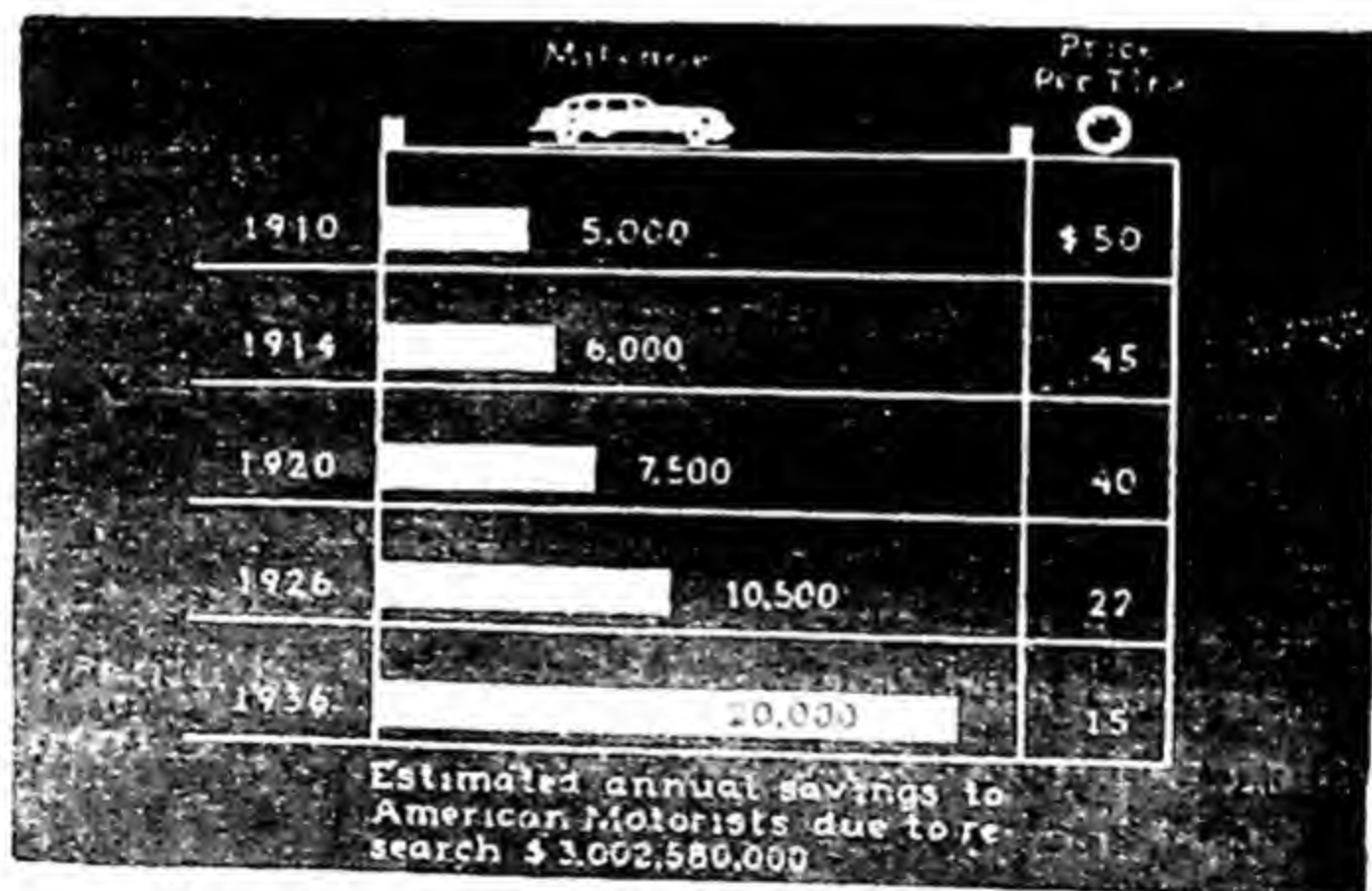


Fig. 1. Chemical research saves you money.

The detection of substances is managed so well by chemists that, for example, one part of poisonous mercury vapor in 20,000,000 parts of air may be recognized by the blackening of paper coated with sensitive selenium sulfide.

Separation of a desired substance from incidental impurities is illustrated well by the winning of gold from the sand or rock in

which it occurs and by the removal of the rare gas krypton from air in which it occurs to the extent of one part in 1,000,000.

The *preparation* of desired substances is so familiar to the chemist that he makes thousands of useful compounds not found in nature.

Problems to be solved are pressing on the chemist from every side. It is only about fifty years since eminent scientists were convinced of the sure and terrible approach of a world wheat famine. Their estimates were based on the exhaustion of then known fertilizer sources. The chemist accepted this challenge and indefinitely postponed the threatened famine by "fixing" the limitless nitrogen of the air, and converting it into fertilizer acceptable to plants — one of the most important achievements of modern science.

The cost of Chilean nitrate fertilizer was cut in half after 1914 by Haber's great research in converting the free nitrogen of the air into useful compounds. We are warned that petroleum will be exhausted in much less than a century, with the result that autos will lack gasoline, ships will lack fuel oil, and modern machinery will lack lubricants. The chemist has already looked ahead to this crisis and now knows how to meet it successfully with the synthesis of liquid fuel from coal. The physicist, chemist, and chemical engineer have given us atomic power.

"Today every fourth worker employed in the United States is at work in industries not in existence, or just starting, in 1900. And every one of these new industries was founded by research." (Clarence Francis.)

In normal years this country spends \$500,000,000 on industrial research, much of it chemical. It is an excellent investment. Chemical research has improved nearly everything about our motor cars and lowered their cost. In a quarter of a century tires were improved to give four times the mileage at one-third the cost. Our personal safety, too, is greater because of safety glass windows and vanadium steel axles.

The vital service of chemistry in war is still fresh in our memory. Super explosives, 100-octane gasoline for military airplanes, fuels to drive rockets 3000 miles per hour, the sulfa drugs,

penicillin, new antimalarials, insect repellents, more effective rat poisons, weed killers, clothing and tents to resist mildew and moisture, plastics for many purposes, special alloys for planes — these are only a fraction of the number of great contributions of chemical research to national safety. The epoch-making development of atomic power is an achievement shared by physics and chemistry. Most of these discoveries are now turned to peaceful service to humanity.

“Seeing tomorrow in the test tube” is a good slogan. In 1941 we, in the United States, consumed \$10,000,000,000 worth of products unknown in 1918. Research, much of it chemical, gave us this new wealth. Chemical industry accounts for \$10,000,000,000 worth of products annually.

“Our frontiers of today are the frontiers of science.” (T. M. Girdler.)

Physics is largely a study of the various forms of energy such as light, heat, electricity, sound, mechanical energy, etc., while *chemistry* deals more with matter. However, each science finds it necessary to include both matter and energy in its field. Chemistry, like physics, is universal.

Energy Transformations. The relation between matter and energy is very close. Matter is difficult to define with exactness, but we usually consider matter as anything that has mass or weight and that occupies space.

The term “*energy*” is applied to the capacity for doing work or to anything that may take the form of motion against an opposing force. Therefore light, heat, motion, and electricity are forms of energy. Chemical energy locked up in substances and the potential energy due to elevated position of bodies (such as a car on the top of a steep hill) are familiar and useful to all of us.

The free *transformation* of one form of *energy* to another is vital to our existence and welfare. Chemical energy stored up in coal may be released as heat just as truly as the chemical energy contained in our food may be converted into the motion and heat of our animal bodies. When the composition of a given portion of matter is changed, energy may be released; yet, conversely, light, heat, and electrical energy may be applied to a portion of matter

so as to force a change in composition. Heating limestone in the kiln changes it into lime and carbon dioxide. Light reduces the sensitive silver bromide on a photographic plate to metallic silver and bromine, and light also causes the dye in wallpaper and curtains to fade. A sharp blow decomposes nitroglycerine (although to be exact, it merely starts decomposition; infinitely more energy is released than can be attributed to the sharp blow). A direct current of electricity decomposes silver salts in solution, depositing metallic silver on objects to be plated.

In this country the amount of electrical energy used increased fivefold in the period between the last two wars — a quarter century. However, the potential power in all our motor vehicles is now 30 times that of all central electrical power stations. This potential power is derived from the chemical energy of gasoline.

The Law of the Conservation of Energy, that *in all ordinary transformations energy is neither created nor destroyed*, is merely a generalized statement of a great many observations. We now know that there are some extraordinary transformations of matter into energy and energy into matter. There is strong evidence that some of the mass of the sun is lost only to reappear as radiant energy.

“Science is founded upon a belief that the world is reliable in its operation.”
(Arthur Compton.)

Substances. A *substance* is a particular kind of material with specific properties, such as gold, sugar, common salt, or sulfur; while a *body* is merely a definite portion of material such as a bottle, a kettle, a stove, or a statue. A bottle may be shaped from the mixture of substances called glass, a kettle from the substance copper, a stove from the substance iron, and a statue from the substance marble; yet the glass could be shaped into a kettle or statue, and the marble into a bottle. Evidently, then, shape and size do not identify glass, although they may well serve in classifying bottles.

Elementary Substances. Substances that we can decompose into two or more simpler substances are called *compounds*. We recognize limestone as a compound substance because on being

heated in the limekiln it breaks down into quicklime and carbon dioxide. Red mercuric oxide when heated is decomposed into the colorless gas oxygen and the metal mercury. Hence mercuric oxide also is a compound. There are nearly five hundred thousand known compounds and millions of new ones can be made when desired.

An element is a substance that cannot be decomposed into two or more substances by our present ordinary chemical methods. While making this flat statement we must admit that methods at



Fig. 2. Heating mercuric oxide to obtain oxygen.

present unknown may become the common methods of the future. Until 1808 quicklime, now recognized as calcium oxide, was called an element but in that year Sir Humphry Davy prepared calcium and showed that it unites with oxygen of pure dry air to form a white solid identical with quicklime. There was then no denying that quicklime could be prepared by union of two simpler substances, and is, in fact, a compound of calcium and oxygen. Familiar examples of elements are iron, copper, oxygen,

gold, mercury, sulfur, and carbon. About ten of the elements are gases; mercury and bromine are liquids, and the rest are solids at ordinary temperatures.

The fact that radium is constantly giving off electrically charged helium atoms does not force us to call radium a compound, for this is no ordinary chemical process. The effects of the cyclotron and of the "atomic pile" in producing atomic changes are also quite extraordinary.

At the beginning of the Christian era the scientific world knew only seven elements -- gold, silver, copper, tin, lead, iron, and mercury (and possibly sulfur). Up to the time of Lavoisier, 1750, only seventeen were known.

Although now, ninety-six elements are known, many of them are unusual. Oxygen in its compounds makes up one-half the

known crust of the earth and silicon one-fourth. Fully 96 per cent of the mass of meteorites is due to iron, oxygen, magnesium, and silicon.

The Peary meteor found in Greenland and now resting in the Museum of Natural History, New York, weighs 36 tons and is worth several million dollars, as a museum specimen. The one that hit Arizona ages ago and exploded into fragments probably weighed 10,000,000 tons.

It takes seventy-four elements to make up one per cent of the earth's crust. The great majority of chemists have never seen nor worked with all the elements; in fact some of the elements are

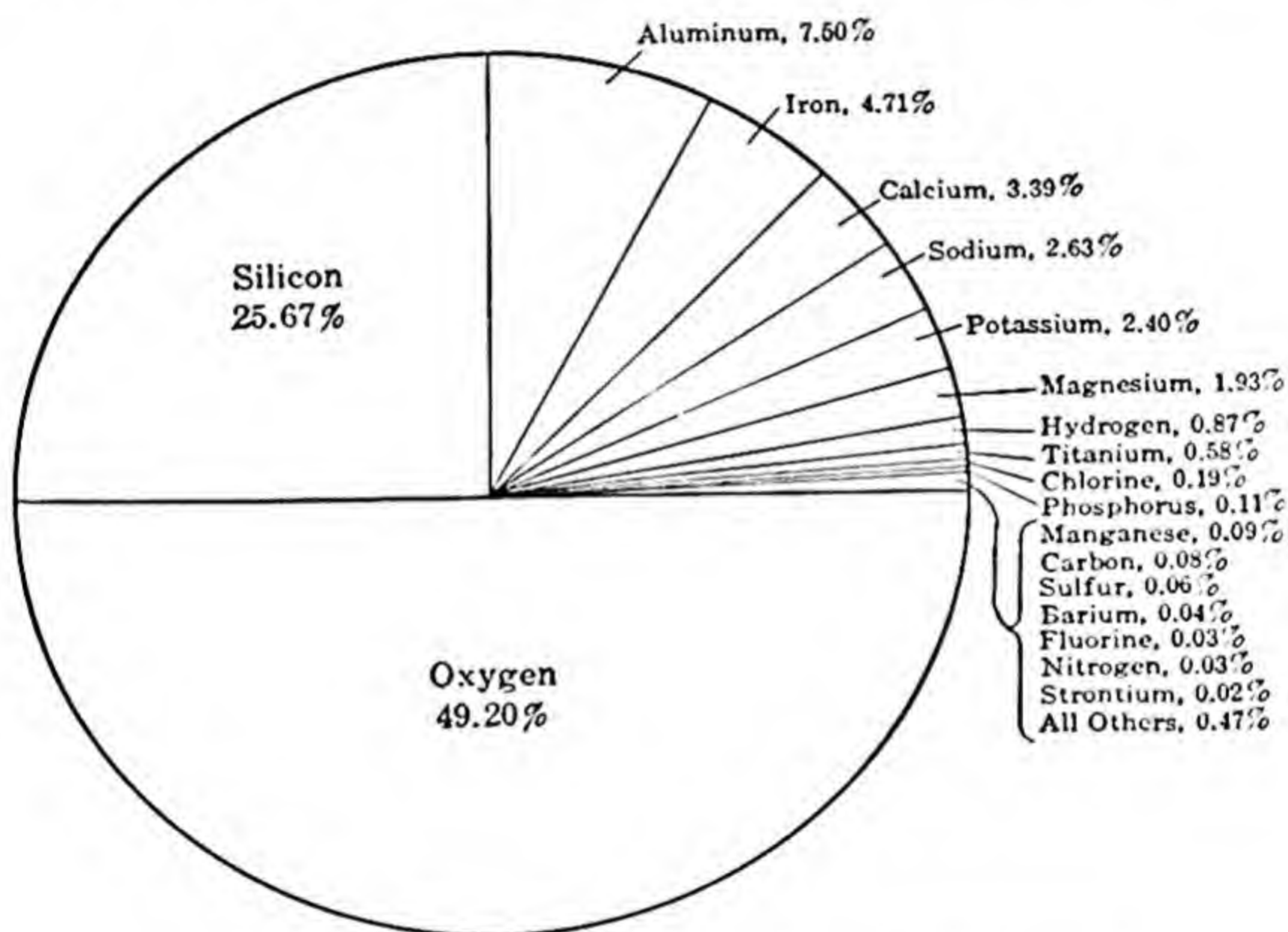


Fig. 3. Percentage of the elements in the earth's crust.

mere curiosities with no known use. But there is always the exciting possibility that the museum specimen of today may become of invaluable service to the world tomorrow. How short a time it has been since tungsten was of little consequence and radium unknown! Neon, an inert gas which Sir William Ramsay

found in the air in the proportion of one part in 65,000, had only academic interest until we recently began to employ neon lighting tubes for beacons and advertising. Their pink-orange glow is penetrating and arresting.

Exercise

1. Aluminum is now made from bauxite ore, yet common clay is rich in this metal. Why, then, does aluminum cost much more than iron, although more abundant in the earth's crust?

Properties. To identify different substances we must know, not size and shape, but such characteristics or properties as *color, odor, taste, hardness, crystalline form, melting point, boiling point, density, solubility* in water or in other solvents, ability to *conduct electricity, index of refraction*, and *chemical activity*. We even may ask if the given substance burns in the air. The student readily recognizes sulfur as such because it is a yellow solid found in nature in rhombic crystals, melting at about 115°C ., insoluble in water but soluble in carbon disulfide. If still undecided, he burns it in the air, notes the blue flame, and throws aside all doubts after one breath of the choking gas formed. In recognizing lead a student is particularly interested in its softness and its low melting point. Sugar he knows at once by its sweet taste, although indiscriminate tasting is not recommended. Hydrogen sulfide once smelled is never forgotten and never separated from the thought of rotten eggs.

In fact we pay money for specific properties of substances. Copper would not sell for fifteen cents a pound to the amount of over a million tons yearly if it were not such an excellent conductor of electricity. Platinum is valuable chiefly because it is so lazy chemically, and is not abundant. Obviously, if glass were opaque or if it dissolved readily in water, it would have no market for use as window panes. If rubber were not resilient the auto would not be popular. Perfect diamonds are valued for sparkle (and scarcity); but crude industrial diamonds, because of their *hardness*, are of far greater importance in the role of abrasive material for cutting and grinding.

Chemists always are trying to improve the useful properties of matter: to make stronger steels and lighter alloys; better synthetic fibers and more powerful explosives; better medicines, and better and cheaper fuels.

2. How did the invention of the *wheel* revolutionize human life?
3. How did the capture and control of fire serve man as a tool?
4. How do you recognize copper, lead, paraffin, salt, vinegar, ammonia, water, alcohol, gold, silver, soap, gasoline?
5. What properties make rubber useful? Gold? Diamonds? Water? Asphalt? Copper? Glass?

Changes. Changes in properties seem to be necessary to life itself. Earth, air, and water are transformed by nature's chemical processes into green grass, trees, flowers, and yet each year these beautiful new products decay and return to earth, air, and water. Iron in moist air rusts with a sharp change in properties, but the change is not hopeless, for great quantities of rusty old iron and steel are annually sent to steel mills to be converted into good steel. All of the rust is changed chemically.

When a platinum wire is heated highly, only a few properties change. The color changes from silver white to red as the temperature rises, but the hot platinum differs in few other respects from cold platinum. Moreover, on cooling, all of its usual properties are resumed. A *physical change* has taken place.

If pure white sugar is heated to a high temperature, it turns black and gives off steam. The black cinder left no longer tastes sweet nor will it dissolve in water. In fact nearly all the properties of the sugar are changed. The student cannot mix the steam and the black cinder (carbon) with any prospect of combining them into the sugar whence they came. The change is *chemical* and, in this instance, hopelessly permanent. None of the resulting products have the same composition as the sugar, nor the same properties. New substances have been formed.

A *physical change* is a more or less temporary change in certain properties such as color, density, conduction of electricity, and ductility. When the original conditions are restored, the original properties return.

Copper may be melted without any change in composition; on cooling to the solid form all of its usual properties are restored. Such a change is purely physical.

A **chemical change** is a very definite change of certain properties with *formation of new substances* and is always accompanied by a gain or loss of energy. Whenever a chemical change takes place we have a *chemical reaction*.

There are, however, some chemical changes in which the new substances formed may, under proper conditions, react to form the original substances. They will be discussed in a later chapter.

Lavoisier as early as 1785 believed that ***in chemical reactions the mass of the system is not changed***. (Law of Conservation of Mass.) Naturally this belief came from careful weighing of the reacting materials and *all* the products. In the instance of burning wood the gaseous products as well as the ashes must be caught and weighed.

Landolt demonstrated the above law with a sealed glass tube shaped like a V. After one of the reacting substances had been introduced into one leg of the tube and the other into the second leg, the tube was sealed, cooled, accurately weighed, and then tilted so as to mix the two reagents. After restoring the original temperature the tube with its contents (a complete system) was again weighed. Within the limits of human experimental error there was no change in weight. Reaction evidently consists in rearrangement of constituent elements.

Measurement. The metric system of measurement (Appendix) is used by scientists and should be used by our general public.

METRIC AND ENGLISH SYSTEMS

1000 millimeters (mm.)	= 1 meter = 39.37 inches
100 centimeters (cm.)	= 1 meter
10 millimeters	= 1 cm.
1000 milliliters (ml.)	= 1 liter = 1000.027 cubic centimeters (cc.)
1.0567 quarts (U.S.)	= 1 liter
1 kilogram (kg.)	= 1000 grams (g.) = 2.2046 lbs.
1 kg. of pure water at maximum density	= 1 liter
1 g. of pure water at maximum density	= 1 ml.

It will be noted here that 1 ml. is practically, but not precisely, the same as 1 cc.

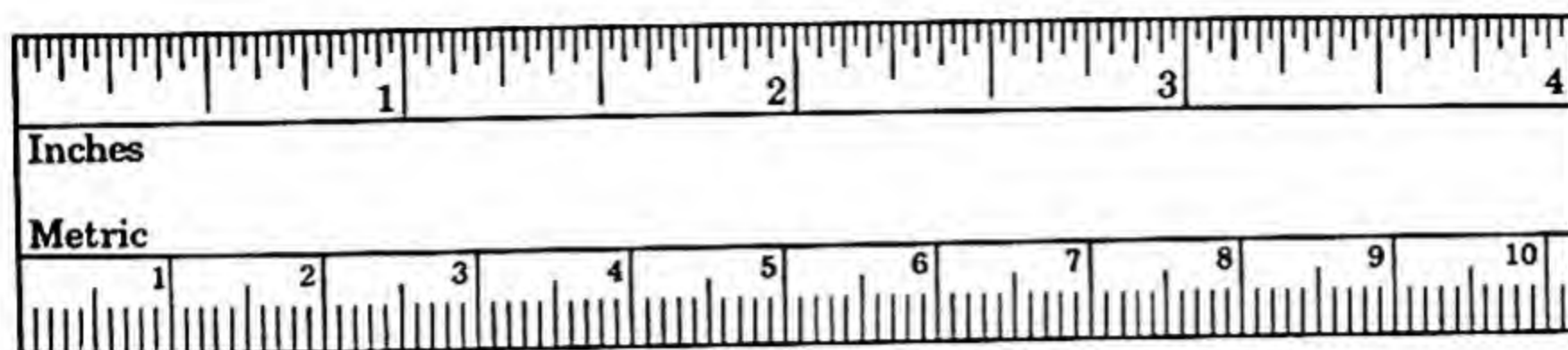


Fig. 4. Comparison of linear units in the metric and English systems.

Accuracy, sometimes extreme accuracy, of measurement is fundamental to scientific progress. Extremely small units of measurement are often found convenient:

1 micron (1μ)	= 1 thousandth of 1 millimeter
1 millimicron ($1\text{ m}\mu$)	= 1 millionth of 1 millimeter
1 Ångstrom (1 Å.)	= 0.1 of $1\text{ m}\mu$
1 microgram	= 0.001 milligram (often called 1 gamma)

Even $1/1000$ of a second is vital — if you are photographing falling drops with a stroboscopic camera whose shutter clicks 1000 times a second. A one-millionth of a second exposure has been used in photography.

Ball bearings for aircraft instruments are now made and measured to one-millionth of an inch.

Quantitative analysis measures percentage composition, thus aiding chemical control of industrial products and greatly facilitating research.

Babcock's invention of the centrifuge method of determining (measuring) the percentage of fat in milk put the dairy industry on a scientific basis.

Scientific Reasoning. Many illustrations of sound reasoning will follow later but here is an interesting example of faulty reasoning:

“Van Helmont planted a willow in a weighed quantity of dry earth, supplied it with water only, and at the end of five years found that it had gained 164 pounds in weight, while the earth had lost only 2 ounces. Here was ingenious proof that practically all the new substance of the willow was made of water — convincing proof — until one hundred years later Ingenhousz and

Priestley showed that plants absorb carbon from carbon dioxide in the air."

The scientific method of work involves careful observation of all pertinent facts, classification of these observations, formulation of an explanation (theory), and testing of the theory by experiment.

Exercises

6. What is the diameter in inches of a 75 mm. gun? Convert one gallon into liters. What is the weight in grams of this volume of water?
7. Is granite a mixture or compound? How about brass, flour, iron rust, sugar, ice cream, and wine?
8. In general, how do you distinguish between compounds and mixtures?
9. What type of change takes place when water freezes? When lard melts? When iron rusts? When a loaf of bread is scorched? When coal burns?
10. What type of change is observed when a rubber band is stretched? When a rubber band is burned?
11. Define a body, a substance, a compound, an element, a chemical reaction.
12. Canners throw fresh peas into a brine of water and common salt. How does this promote separation of good from bad?
13. When sand, lime, and soda are fused together to form glass, is the change physical or chemical?
14. If, while camping in the wilds, you upset all the salt on a white sandy beach, what would you do to recover the precious salt?
15. Convert two gallons to liters.
16. How many meters in a mile?
17. Convert four pounds into grams.
18. What is the weight in grams of one gallon of water? See Appendix for data.
19. How could you separate a mixture of oxygen and ammonia? Ammonia is very soluble in water.
20. A Sharples super-centrifuge at 50,000 rotations per minute multiplies the ordinary force of gravity 62,000 times. What fraction of a ton would a silver half dollar (ordinary weight 12.58 grams) weigh while so whirled by this centrifuge?

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Chapter 2 THE COMPOSITION OF PURE SUBSTANCES

Pure Substances and the Law of Definite Composition.¹

Every pure compound has a definite composition by weight. Common water from any portion of the earth, if pure, is composed of hydrogen and oxygen in the proportion of 1 part of hydrogen to 7.94 parts of oxygen by weight. If other elements are present, they represent impurities and can readily be separated from the water. Any mixture of alcohol and water might look like water, but it would not be a pure substance. It would not boil at 100° C. under one atmosphere pressure as does water, nor would it act chemically towards other substances exactly as does water. Sugar and clean white sand might be mixed very deceptively, but the analysis would show a very different composition from that of sugar. Such a material would not be a pure substance. If the sand were removed (How could you do it?), the remaining sugar would have the same percentage of carbon, hydrogen, and oxygen as any other specimen of pure sugar.

The difference between pure compounds and mechanical mixtures is evident from this *Law of Definite Composition*. *The proportions in any mechanical mixture may be varied considerably without any abrupt change in properties*, as in the sand-sugar material, but if the proportions of carbon, hydrogen, and oxygen in pure sugar were changed, the substance would no longer be sugar. As a matter of fact, alcohol is composed of the same elements as sugar and can be made from it, but the percentage composition is different. Thousands of pure substances contain only these three elements, but in each case either the proportion or the arrangement of

¹ Often called the *Law of Definite Proportions*.

these elements is different. The formation of compounds is always attended by a pronounced energy change. Not so with mere mixtures.

In a mixture the properties are the sum of the properties of the constituents, as demonstrated so tastefully in a well-flavored soup. The properties of a compound, however, are nearly independent of the properties of the substances used in making it.

Joseph Black in England (1755) made the first quantitative studies of chemical changes, the first studies in which the materials taking part in those changes were accurately weighed or measured.

Early in the nineteenth century many chemists believed and taught that a compound contains its elements in a series of ratios, varying according to its location or manner of preparation.

The attack on this theory was led by Joseph L. Proust, of Madrid. Berthollet, in Paris, defended it by citing instances in which compounds seemingly varied in composition according to where they were obtained, or how prepared. In each case Proust was able to show that Berthollet's samples were so seriously at fault that the inference was valueless. He was further able to show that a purified compound has a fixed composition and uniform properties regardless of where it was obtained or how prepared.

A classic illustration of the difference between a mechanical mixture and a chemical compound is found in an experiment with iron and sulfur. If very fine iron filings are mixed with powdered sulfur, it may be shown that the sulfur still retains its own characteristic properties, as does the iron, and that each may be removed by simple mechanical means. A magnet attracts the iron as if the sulfur were not present. Carbon disulfide dissolves the sulfur out of the mixture as if the iron were not present and, on filtration, a clear solution (the filtrate) is obtained. This yields the sulfur if allowed to evaporate.

If the mixture of iron and sulfur is heated in a test tube, interesting color changes are observed. Finally the mixture glows brightly, even after it is removed from the flame. Evidently heat is given off by some sort of action between the two elements. After there is no further change a black solid is obtained which is not attracted by the magnet and from which sulfur is not dissolved by carbon disulfide. The conclusion is that neither free iron nor free sulfur is present, and that they have combined to form a compound. A reaction took place which, when well started, gave off considerable heat.

The experiment goes as described if the two elements are taken in a very definite proportion. If more iron than is called for by that proportion is used, some free iron is left over and may be removed, leaving the pure product of the reaction. If more sulfur than is called for is used, some sulfur is left over and may be removed. The hard black solid obtained in the above experiment is a compound called iron sulfide. It has several properties quite different from those of iron or sulfur.

This and similar experiments force us to believe that elements react in very definite proportions to form compounds. A logical next step is an effort to learn what these proportions are, especially in reactions involving oxygen, the great central element.

Combining Proportions. The Law of Definite Composition created an interest in the *ratio* of the weights of elements combined in a pure compound. These combining weight ratios are easily calculated from the analysis of pure compounds. Since most elements unite directly with oxygen, it is possible to learn from actual experiment what weight of each element will combine directly with a fixed weight of oxygen. These numbers may then be compared.

In the following table are listed the relative weights in which some of the elements combine with eight grams of oxygen, a very convenient weight for it gives a value of practically one to the lightest of all elements, hydrogen:

SUBSTANCE	PERCENTAGE COMPOSITION BY ANALYSIS		NUMBER OF GRAMS OF THE ELEMENT UNITING WITH 8 GRAMS OF OXYGEN
Magnesium oxide	Magnesium	60.32	12.16
	Oxygen	39.68	
Copper oxide	Copper	79.9	31.80
	Oxygen	20.1	
Water	Hydrogen	11.19	1.008
	Oxygen	88.81	
Aluminum oxide	Aluminum	52.94	9.00
	Oxygen	47.06	
Carbon dioxide	Carbon	27.27	3.00
	Oxygen	72.73	
Calcium oxide	Calcium	71.43	20.03
	Oxygen	28.57	

From this table a partial list of combining proportions may be derived:

Oxygen	= 8.0	Hydrogen	= 1.008
Magnesium	= 12.16	Aluminum	= 9.0
Copper	= 31.8	Carbon	= 3.0
Calcium	= 20.03		

Since 1.008 g. of hydrogen are evidently equivalent in combining value (as in water) to 8 g. of oxygen, it might be conjectured that the weight of any element uniting with 1.008 g. of hydrogen would probably unite (if at all) with exactly 8 g. of oxygen. In the case of chlorine, 35.46 g. unite exactly with 1.008 g. of hydrogen, and, true to the above assumption, 35.46 g. of chlorine unite with 8 g. of oxygen.

Exercise

1. Predict how many grams of magnesium combine with 35.46 g. of chlorine. How many grams of aluminum, and of copper, unite with 35.46 g. of chlorine?

It is evidently reasonable to state that *a combining weight of any element is the number of grams of that element that combine with 8 g. of oxygen.*

Law of Multiple Proportions. Since there are instances where two elements combine in different proportions to form a series of compounds, we may suspect that it is possible for some elements to have at least two combining weights. The two oxides of carbon illustrate this fact.

	OXYGEN	CARBON
Carbon dioxide	8 g.	3 g. (= 1×3 g.)
Carbon monoxide	8 g.	6 g. (= 2×3 g.)

The two oxides of hydrogen may also be cited.

	HYDROGEN	OXYGEN
Water	1.008 g.	8 g. (= 1×8 g.)
Hydrogen peroxide	1.008 g.	16 g. (= 2×8 g.)

The five oxides of nitrogen are radically different in properties, yet all contain only nitrogen and oxygen:

	NITROGEN	OXYGEN
Nitrous oxide	14 g.	8 g. ($= 1 \times 8$ g.)
Nitric oxide	14 g.	16 g. ($= 2 \times 8$ g.)
Nitrogen trioxide	14 g.	24 g. ($= 3 \times 8$ g.)
Nitrogen tetroxide	14 g.	32 g. ($= 4 \times 8$ g.)
Nitrogen pentoxide	14 g.	40 g. ($= 5 \times 8$ g.)

It is evident that the elements combine in the ratio of their combining weights or simple whole multiples of these. *The Law of Multiple Proportions* (a mere generalization) is often stated as follows: *If two or more elements form a series of compounds, the different weights of one which combine with a definite weight of another stand to each other in the ratio of small whole numbers.*

For certain compounds of carbon (organic compounds) the whole numbers are not always "small."

Determination of Combining Weights. There are at least four general methods of determining the combining weights of elements:

1. Combination of the element with oxygen. Cautious heating of weighed magnesium in air yields magnesium oxide which can be weighed. Subtraction of the weight of magnesium from the weight of the oxide gives the weight of oxygen combined.

2. Decomposition, by heat, of a pure oxide, when possible. Silver oxide is decomposed into its elements at about 250° C. The oxide of calcium, quicklime, is too stable to decompose at that temperature.

3. Reduction of a hot metallic oxide by hydrogen. This is possible only with less active metals such as copper and iron. Again calcium oxide would not yield its oxygen.

4. Displacement of hydrogen from an acid by an active metal, zinc, for example.

Determination of the Combining Weight of Magnesium. The combining weight of magnesium relative to oxygen, for

example, may be determined in the laboratory by heating a weighed quantity of this metal in a porcelain crucible. The cover is kept on during the heating, which is gentle at first, but finally reaches the limit of the flame. After cooling, crucible and ash (magnesium oxide) are weighed, heated again, and weighed. The operation is repeated until there is no further gain in weight. After a final weighing the gain in weight due to combination of oxygen of the air with the metal is easily calculated. By means of a simple proportion the number of grams of magnesium reacting with 8 g. of oxygen is found. The fourth method could also be used for magnesium.

Determination of the Combining Weight of Copper. The combining weight of copper may be determined by passing air or pure oxygen through a glass tube containing a weighed amount of heated copper powder. Black copper oxide is formed. Or copper oxide may be torn apart with the aid of hot hydrogen and the loss in weight noted. For example, the student may weigh out black copper oxide in a small porcelain boat or narrow dish and, after placing the boat in a hard-glass tube *D*, pass dried hydrogen gas from the generator *A* through the tube while heating until there is no further change (Fig. 5). The hydrogen unites with all the oxygen of the copper oxide, leaving red copper. The steam formed is driven out through the drying tube *C* by the steady stream of hydrogen which has first been dried by passing through *B*. From the original weight of the copper oxide and the final weight of the copper one can, by simple subtraction, learn the weight of oxygen. Suppose that 1.700 g. of copper combined with 0.420 g. of oxygen, as may be learned by subtracting the weight of the copper from the weight of copper oxide. To learn how

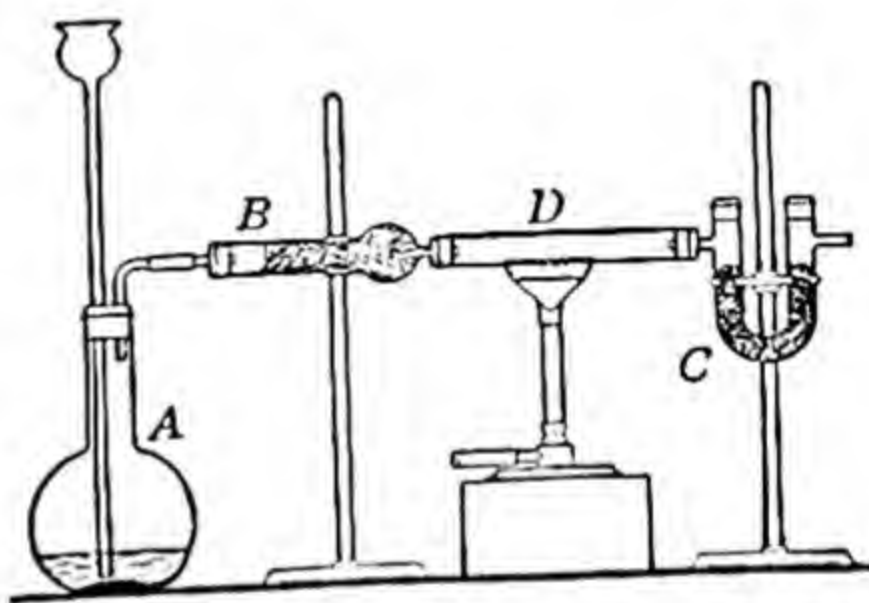


Fig. 5. Reduction of copper oxide in *D* by hydrogen from *A* which has been dried in *B*. The water formed is collected in the weighed drying tube *C*.

many grams of copper would combine with exactly 8 g. of oxygen at this rate, we write a proportion:

1.700 g. copper : 0.420 g. oxygen : : x g. copper : 8 g. oxygen.

Optional

$$\frac{1.700}{0.420} = \frac{x}{8}$$

Solving

$$x = 32.381 \text{ g.}$$

Therefore the combining weight of copper is 32 (approximately).

2. Since the oxygen and hydrogen unite to form water vapor, caught in the weighed drying tube, could you determine by the above experiment how many grams of hydrogen combine with 8 g. of oxygen?

It is difficult to make metals unite with hydrogen, but most metals will displace hydrogen from acids. The number of grams of any metal — zinc, for example — that can take the place of 1.008 grams of hydrogen in an acid is certainly equivalent to the 1.008 grams of hydrogen, for it is combining with the rest of the compound just as did the one gram of hydrogen. For example, since 32.69 g. of zinc displace 1.008 g. of hydrogen from acids, the combining weight of zinc is 32.69 g.

Because the combining weight of many elements varies from compound to compound, as with the five oxides of nitrogen, the combining weight is not the most convenient, although it is useful in determining atomic weights.

With the development of the conception of *atoms* as simple reacting units (following chapter) a table of *atomic weights*, invariable units of quantity, was gradually built up. These have a fundamental relation to combining weights and, indeed, are either equal to or are small multiples of combining weights.

ELEMENT	COMBINING WEIGHT	ATOMIC WEIGHT (APPROXIMATE)
Oxygen	8.	16. (= 2×8)
Hydrogen	1.008	1.008 (= 1×1.008)
Chlorine	35.46	35.46 (= 1×35.46)
Copper	31.8	63.6 (= 2×31.8)
Carbon	3.0	12. (= 4×3)
Sodium	23.	23. (= 1×23)
Aluminum	9.	27. (= 3×9)

In an early chapter detailed methods will be given for the determination of relative weights of atoms. In some instances the

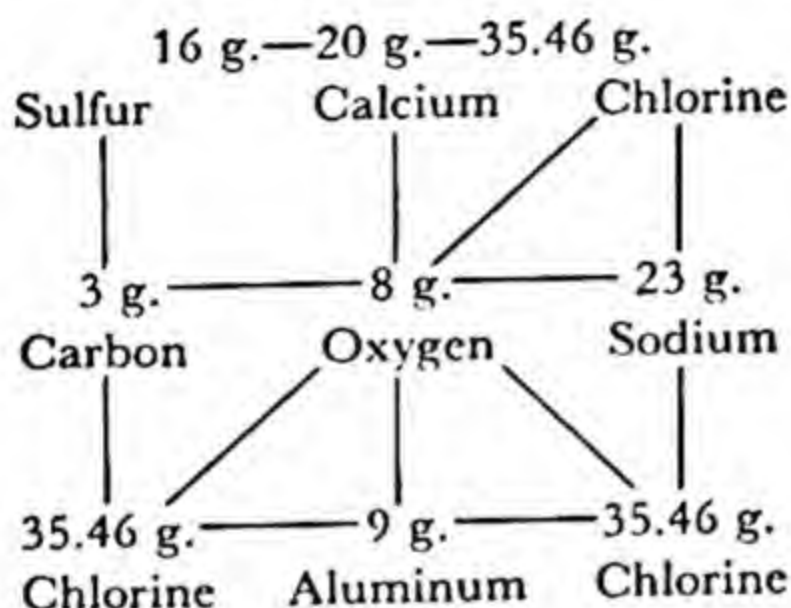
first step may well be a laboratory method of determining the combining weight of the element in question. For the present we may take the weights of different kinds of atoms relative to that of one selected as a standard for comparison: the oxygen atom with an arbitrarily chosen weight of 16. By comparison the weight of one hydrogen atom is 1.008.

The hydrogen atom (lightest) was once set as the standard with an exact atomic weight of 1, but there are fewer experimental errors if oxygen is made the standard.

Exercises

3. The simplest oxide of manganese is 77.44 per cent manganese and 22.56 per cent oxygen. Calculate the combining weight of manganese.
4. The diagram on page 21 shows the number of grams of various elements equivalent (in combining value) to 8 grams of oxygen, and equivalent to each other.

For example, 9 g. of aluminum combine with 35.46 g. of chlorine. In what proportions do carbon and chlorine combine? Sulfur and calcium?



5. Silver oxide contains, by analysis, 93.1 per cent silver and 6.9 per cent oxygen. Calculate the combining weight of silver.
6. In pure barium chloride 65.95 per cent of any weight is barium and 34.05 per cent chlorine. How many grams of barium have combined with 35.46 grams of chlorine, and are equivalent in combining value to this weight of chlorine?
7. The analysis of pure zinc oxide shows 80.34 per cent zinc and 19.66 per cent oxygen. What is the combining weight of zinc?

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Chapter 3 THE ATOMIC THEORY. INTRODUCTION

Ancient Greek Theories of Matter. The divisibility of matter has always been familiar to man, but it remained for the early Greek philosophers, disputing without the wholesome check of laboratory experiment, to set a theoretical limit. The smallest particles of matter conceivable in their wildest flights of imagination they called *atoms*. The conception of atoms as extremely minute, compact, indivisible pellets was held by many scientists for centuries.

On the other hand Aristotle decided that all matter must be made up of at least four elements, *Fire, Earth, Air, and Water*, and possibly a vague fifth, or "*Quintessence*."

The Alchemists. The idea of varying the proportions of these qualities in matter suggested, some centuries after the time of Aristotle, the possible transmutation of one substance into another. Many secret cults, mystical writings, much self-deception and much quackery marked the development of chemistry, or *alchemy*, as it was termed from the third century to the fifteenth or even later.

The art was originally Greek, carried to Alexandria in the golden days of Egyptian learning, preserved by the Arabs, and finally carried by them into Western Europe. The continual struggle to convert base metals into gold enlisted the patronage of kings, who hired their private alchemists to replenish royal treasures. Yet in spite of the lack of order and system alchemy did carry on much knowledge into the Middle Ages.

Dalton's Atomic Theory. The "vague atomistic theories" of ancient Greek philosophers were of little real value and were discarded by 1803. John Dalton, an English scientist, like Higgins a few years earlier, sought an explanation for the facts

described by the laws of definite composition and of multiple proportion. His useful theory may be stated as follows:

1. *The ultimate particles of a pure substance, simple or compound, are alike in size and weight.*

2. *The "simple atoms" of an elementary substance are indivisible, and can neither be created nor destroyed.*

3. *The "compound atoms" of a chemical compound are formed by the union of two or more elementary atoms.*

4. *Combination between atoms takes place in the simplest possible ratios, e.g., one atom of A with one, two, or three atoms of B.*

The smallest particles of these compound substances formed by the union of two or more atoms of different elements, we call *molecules* although Dalton termed them "compound atoms." His theory, although not correct in all details, greatly aided scientific thought for a century.

The *molecule* is the smallest physical unit of a pure substance, with the same percentage composition as any larger amount. For certain exceptions the term "conventional molecule" is convenient. In practice we determine properties in a mass of a great

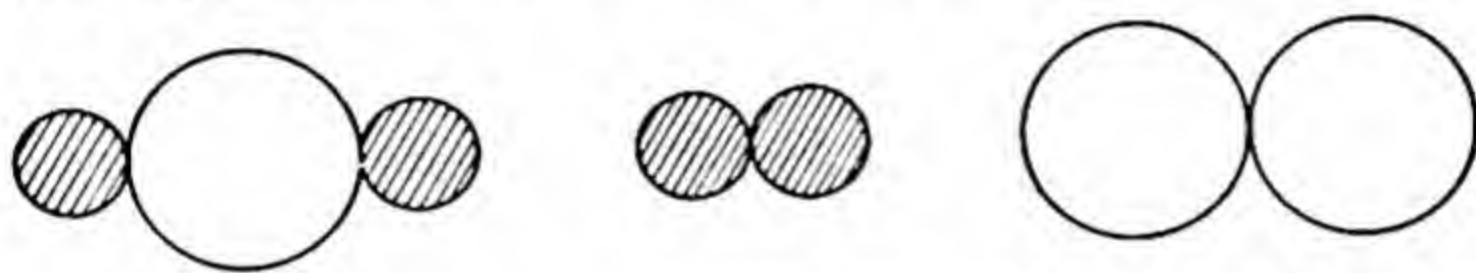


Fig. 6. Dalton's "compound atoms," or molecules, were thought to be composed of elementary atoms of the same kind or of atoms of different kinds.

many molecules. If a molecule of sugar were taken apart, these smaller particles would no longer taste like sugar, they would in fact be atoms of carbon, hydrogen, and oxygen. The smallest particles of elements taking part in chemical reactions we call *atoms*. A reaction, then, is merely a regrouping of the atoms in new combinations. Two or more atoms of the same kind may unite to form molecules of an elementary substance such as oxygen gas.

This theory explains why, during a reaction between substances in a closed vessel, there is neither gain nor loss of weight (*Law of Conservation of Mass*). All the atoms of the reacting substances are accounted for in the new substances.

It explains also the *Law of Definite Composition* for when one element unites with another, the combination always takes place between definite numbers of atoms of each kind. For example, if two atoms of hydrogen unite with one atom of oxygen to form a molecule of water, it follows surely that the percentage of oxygen and hydrogen by weight in pure water is always the same.

It also explains the *Law of Multiple Proportions* (see page 17). When two atoms of hydrogen unite with *two* atoms of oxygen (instead of one, as in water), we should have a new compound quite different from water. Such a compound is known and is called hydrogen peroxide.

We have obtained convincing evidence of the existence of atoms and molecules and have even counted and weighed them. Millikan reports the number of molecules in a milliliter of any gas under standard conditions of temperature and pressure as 2.71×10^{19} , a value closely confirmed by several different methods.

Molecules are so small that if we empty one liter of water into the ocean, with thorough mixing, and then dip out one liter, we will recapture 2220 of the original molecules of water added to the ocean. A row of 40,000,000 molecules in contact would measure one inch.

The Modern Theory of Atomic Structure. Dalton's atomic theory did not explain why some elements react with each other

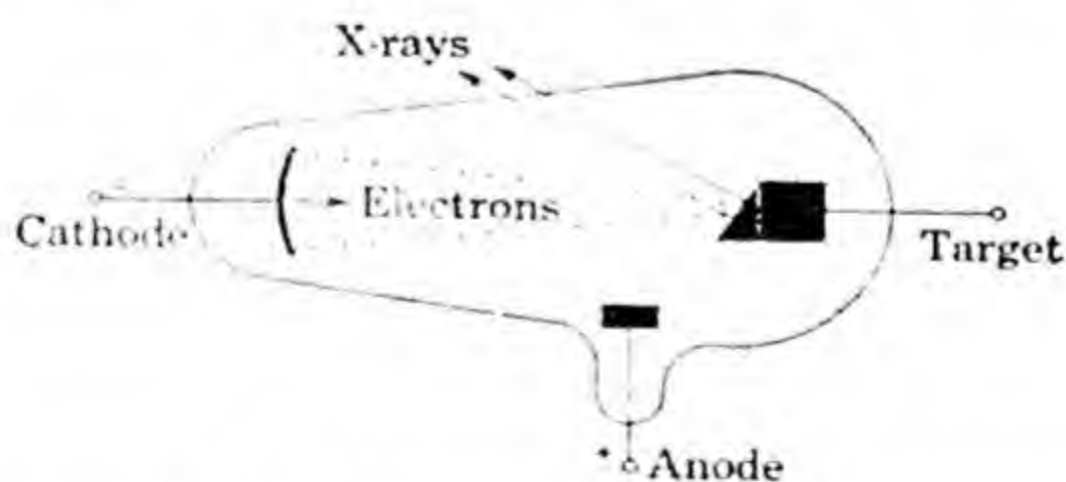


Fig. 7. X-ray tube showing the effect of a stream of electrons (cathode rays) on the metal target. X-rays result.

and others do not, what forces hold atoms together in molecules, and how the constituent atoms are arranged.

About 1879 Sir William Crookes made a study of high-vacuum tubes which conduct electricity at high voltage (Fig. 7). Sealed-in

wires support the anode and cathode. With any gas at a pressure of $\frac{1}{1000}$ of an atmosphere or less, and with any conducting cathode, peculiar radiations called "cathode rays" emanate from the cathode with the velocity of light and cause a greenish fluorescence where they hit the glass wall of the tube. For that matter, they may heat to incandescence a piece of metal such as copper or tungsten interposed in their path as a "target." When a cathode tube is placed between two metal plates, one carrying a heavy positive charge and the other a heavy negative charge, the rays are deflected towards the positive plate. Crookes surmised and J. J. Thomson later proved (1897) that the cathode rays are a stream of negatively charged particles ejected by the electric current. And since these same particles are thrown off from the cathode (or the gas?), no matter what the cathode or gas, they must be constituent parts of atoms of all elements. A heated cathode throws off the electrons better than a cool one.

Thomson named these minute negatively charged particles **electrons** and determined that they have a mass of only $\frac{1}{1837}$ of the mass of the hydrogen atom, the lightest of all atoms. Furthermore, the element radium was found to throw off not only electrons with high velocities, but positively charged particles. This "radioactive disintegration," long supposed to be limited to a very few elements, is a spontaneous process not under our control, in spite of some success with artificial radioactivity.

Out of such work since 1897, including Rutherford's discovery of the **proton** (a positive charge of electricity with a mass practically that of a hydrogen atom) in 1911, has come the modern conception of atomic structure, admittedly incomplete, but based upon many unquestioned facts. *We now feel certain that the ordinary neutral atom is a miniature solar system with a compact central nucleus made up of neutrons (neutral units with the mass of protons) and a number of free protons (positive charges of electricity). Surrounding these are enough planetary electrons to balance electrically the protons in the nucleus.* So small are these three fundamental units, **neutrons**, **electrons**, and **protons**, that the atom is mostly space. So, too, is the solar system.

If the nucleus of an atom were magnified to a two-inch sphere, the nearest electron would be 2000 feet away. The gold atom,

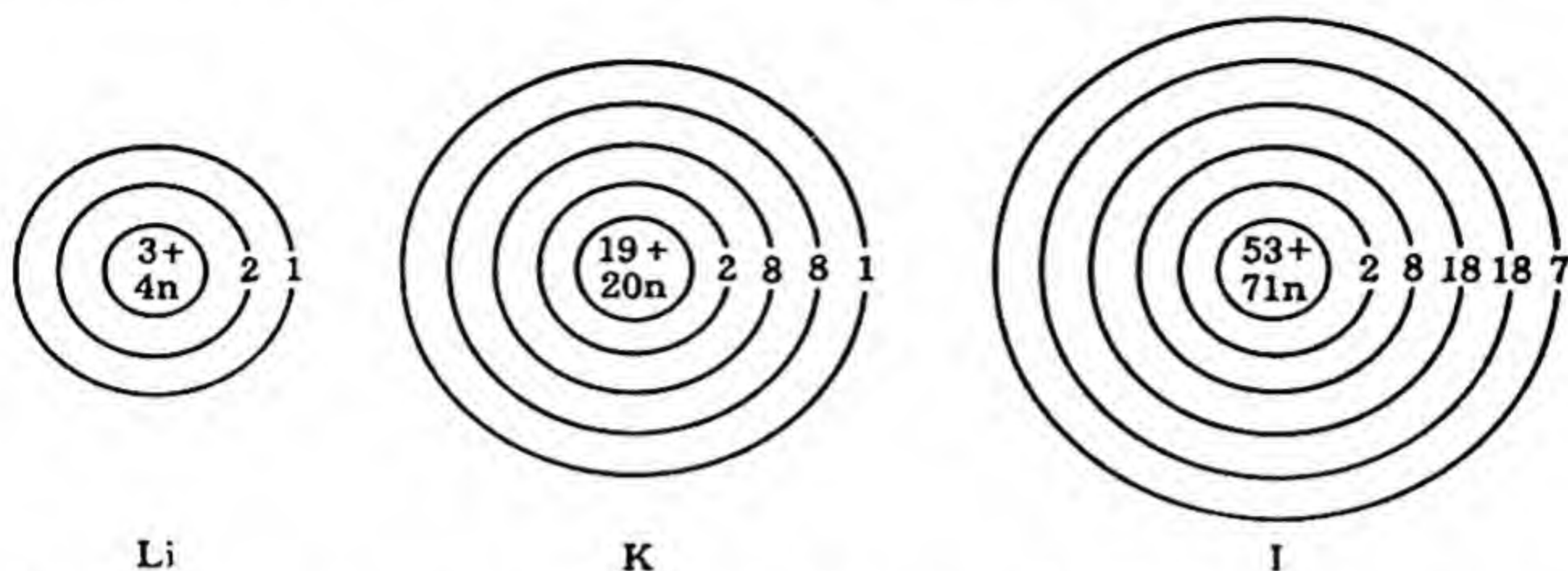


Fig. 8 Atomic structure of three typical elements, Li, K, I, showing number of electrons in the various energy levels or shells.

according to Rutherford, has 100,000 times the diameter of its own nucleus.

In all probability the planetary electrons revolve at great velocities, 150,000 miles per second, around the nucleus, some in circular, and some in elliptical orbits. In addition there is a spinning of each electron to be considered.

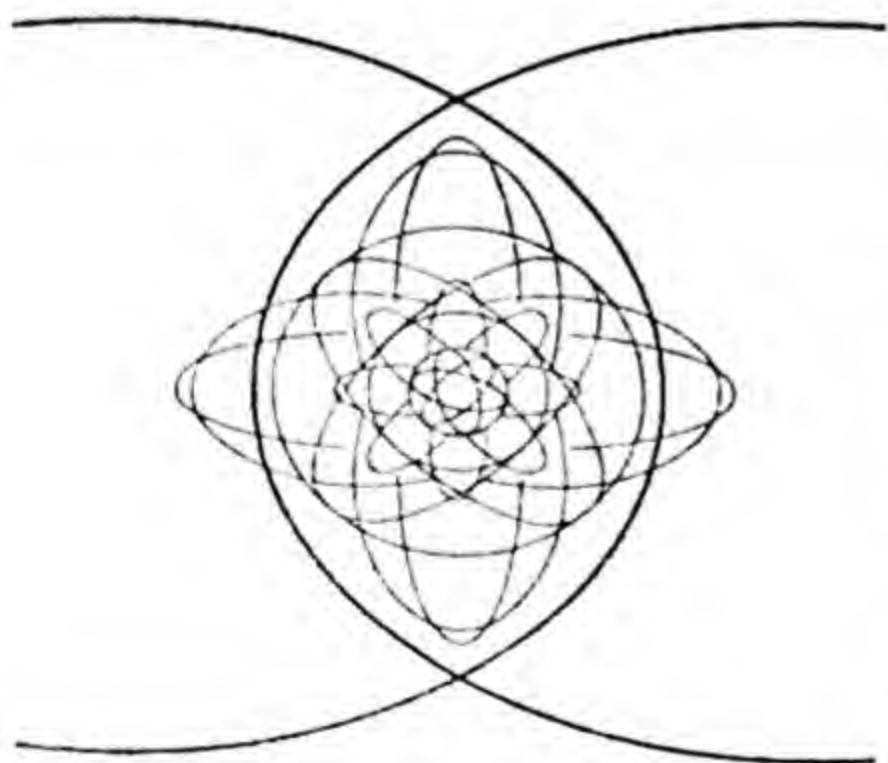


Fig. 9. Complicated electron orbits in the tantalum atom.

The simplest atom is hydrogen, made up of a single proton and a single electron. (One of the most complex atoms is uranium, with 92 protons, 92 electrons, and 146 neutrons.) Since the hydrogen atom weighs 1.008 and the electron mass is only $\frac{1}{1837}$ of the hydrogen mass, it is evident that the proton has a mass of approximately one. In other words, the mass of the

electrons is negligible, and practically all the mass of an atom is concentrated in the nucleus, a relatively minute fraction of the entire volume.

In the white dwarf star, Wolf 457, the weight of a single cubic inch is probably 9000 tons. This must be because the effect of the star's extraordinarily high temperature is to strip planetary electrons from a considerable number of the atoms.

Some constituents of atoms	{	Electrons	{ Negative particles, $\frac{1}{1837}$ of mass of hydrogen atom
		Protons	{ Positive particles of mass 1.008 (all that is left when a hydrogen atom loses its single electron)
		Neutrons	{ Uncharged particles of mass 1.008 (same mass as a proton)

It is helpful at this stage to note that with many of the commonly-met atoms the outer shell of electrons may contain from one to eight electrons. In chemical reactions this number usually is raised to eight either by a transfer of electrons from another atom (electrovalence) or by a sharing process (covalence).

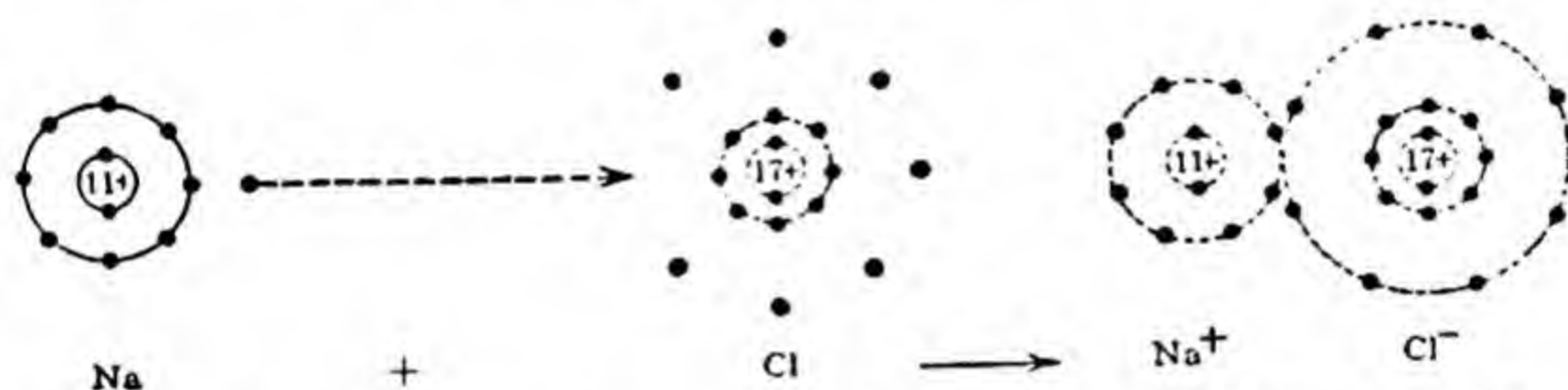
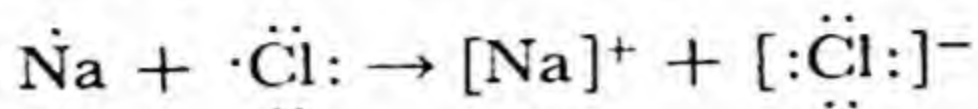


Fig. 10. Reaction between sodium and chlorine, showing electron transfer.

Although the electrons (negative) are attracted by the nuclear protons (positive), some of the outer planetary electrons are known to escape to other atoms. Curiously enough some of the most active atoms, like those of the metals potassium and sodium, have a very great tendency to give away outer electrons, while some of the most active non-metallic atoms like those of chlorine and fluorine exhibit a reluctance to give away electrons, but show an eagerness to take on electrons. Now we understand why two such active elements as potassium and sodium can refuse to react with each other. Each of these two types of atoms is willing to yield an electron to an "acceptor." For this reason, sodium reacts with chlorine, because the chlorine atom eagerly takes on the electron that the sodium atom is so willing to discard. Chem-

ical reaction takes place and a molecule of sodium chloride, common salt, is formed. If we consider only the outer electrons the reaction can be represented as follows:



The loss of a negative electron from an electrically neutral sodium atom leaves an excess of one proton (or gives a positive charge) to that atom, while the gain of an electron by a neutral chlorine atom confers a negative charge on that atom. Consequently the two oppositely charged atoms are held together in the molecule of salt by electric attraction. (In some types of reaction outer planetary electrons in pairs are shared by atoms which are so held together.) Metallic atoms tend to lose electrons, non-metallic atoms to gain them.

The atoms of the inert elements, like helium, neon, and argon, are so stable that they neither gain nor lose planetary electrons, consequently they never react with anything, and form no compounds at all. (See argon as a possible exception.)

Electron Tubes. In the evacuated radio tube (represented diagrammatically by Fig. 11) electrons are "boiled out" of the metal filament which is heated by an electric current. The process is reminiscent of the evaporation of molecules of water from the surface when the liquid is heated.

The flying electrons are attracted by the positively charged plate and reach it except when the open-mesh grid is given sufficient negative charge to repel electrons. This grid is connected to the wireless antenna so that rapidly pulsating electric current charges caused by the signals increase and decrease the amount of negative charge on the grid thousands of times per second. In turn the electron streams in the tube are allowed to pass through holes in the grid, are stopped, etc., with variations reproducible, after magnification of current, in the loud speaker.

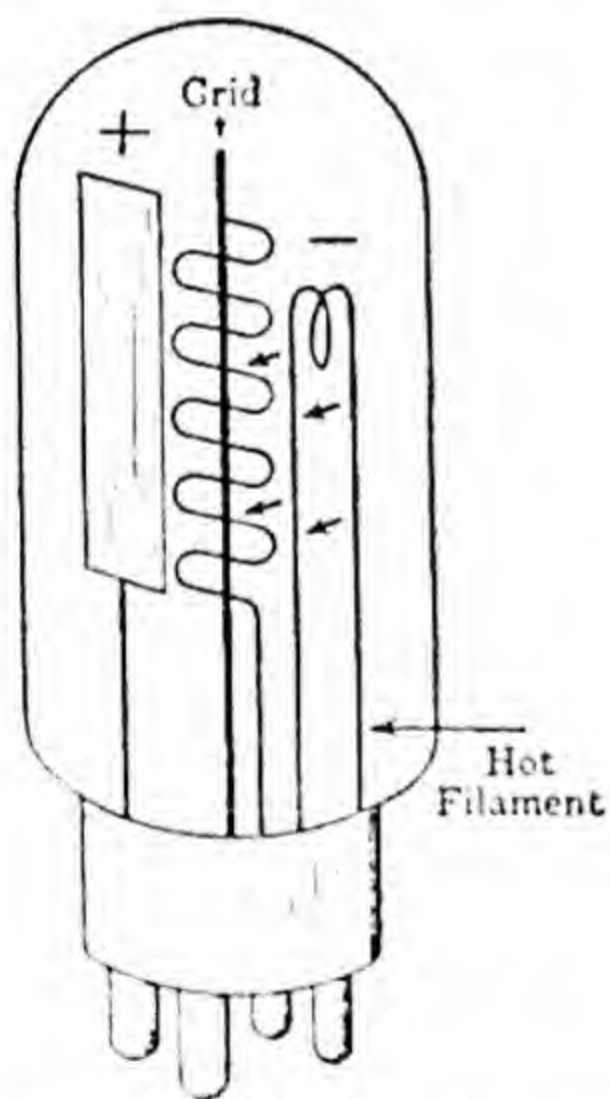


Fig. 11. Radio tube with electrons thrown out by the heat of the filament, varied in intensity by the grid, and caught by the plate.

It is interesting to note that a hot wire throws off electrons (radio tube), a flame shakes outer electrons from molecules in air (making it conducting) and light shining on the more active metals such as cesium and potassium in a vacuum tube forces the escape of electrons from such metallic surfaces (photoelectric effect used in sound films of the movies). Some tubes of this latter type can detect pinholes in steel plate racing through a mill at 1000 feet a minute. This is the "electric eye" that opens doors, counts passing objects and is generally useful.

If the anode in such an electron tube as Fig. 11 (without a grid) is made of a material that does not readily emit electrons, current from any power source can flow in only one direction through the electron tube. Thus alternating currents of electricity can be "rectified" to direct current.

In grid tubes the flow of current can be controlled through change in the charge on the grid. Thus electrical circuits can be opened, closed, modified or measured.

Karl T. Compton says, "It has been calculated that the energy of a transatlantic radio signal caught by the receiving station in Newfoundland comes in at about the rate required to lift a fly 7 inches in a year."

In the electron microscope, far more powerful than the best compound microscope, streams of electrons are focussed by a magnetic field.

Exercises

1. State Dalton's Atomic Theory.
2. Define an atom, a molecule, an electron, a proton, a neutron, and a nucleus.
3. What changes have been made in Dalton's Atomic Theory to bring it up to date?
4. What are the sources of electrons?
5. How does sodium react with chlorine?
6. If a neutral atom contained 40 protons as well as many neutrons in the nucleus how many electrons must be present? Where are those electrons?
7. How many molecules are there in a liter of any gas measured under the usual standard conditions of temperature and pressure?
8. Why should potassium and chlorine atoms react with each other while potassium and sodium do not?

9. Why is there no measurable gain or loss in weight during a chemical reaction?
10. What evidence have we that negatively charged particles are among the constituents of all atoms?

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Chapter Outline

1. The Greek Atom.
Aristotle's four elements.
2. Dalton's Atomic Theory.
Are all atoms alike?
How far can a molecule be subdivided?
Relation of atoms to molecules?
What is a chemical reaction?
How does Dalton's theory explain the laws of Definite Composition and of Multiple Proportion?
Had the atomic theory been overthrown after a century, would chemistry have lost a century of progress?
How small are molecules?
3. The Modern Atom.
What is a Crookes tube?
What are cathode rays?
Proof that there are electrons in all atoms.
The proton.
The neutron.
Relative weights of the proton and the electron.
The nucleus of the atom.
The planetary electrons.
How can an atom be neutral when it is made up of charges of electricity?
How does sodium react with chlorine?
What holds these atoms together after reaction?
Nature of a current of electricity.
Radio electrons.
Uses of electron tubes.

Later the student should prepare his own Chapter Outline as an aid to study.

Chapter 4 SYMBOLS, FORMULAS, AND EQUATIONS

Symbols and Formulas. Up to the time of Berzelius, about a century ago, chemists used strange symbols for the elements. The moon ☾ represented silver, Δ was the symbol for water, ♀ stood for copper, and \triangleplus for sulfur. But these were supplanted at Berzelius' suggestion that one or two significant letters of the Latin name of the element be used. Thus the symbol for carbon

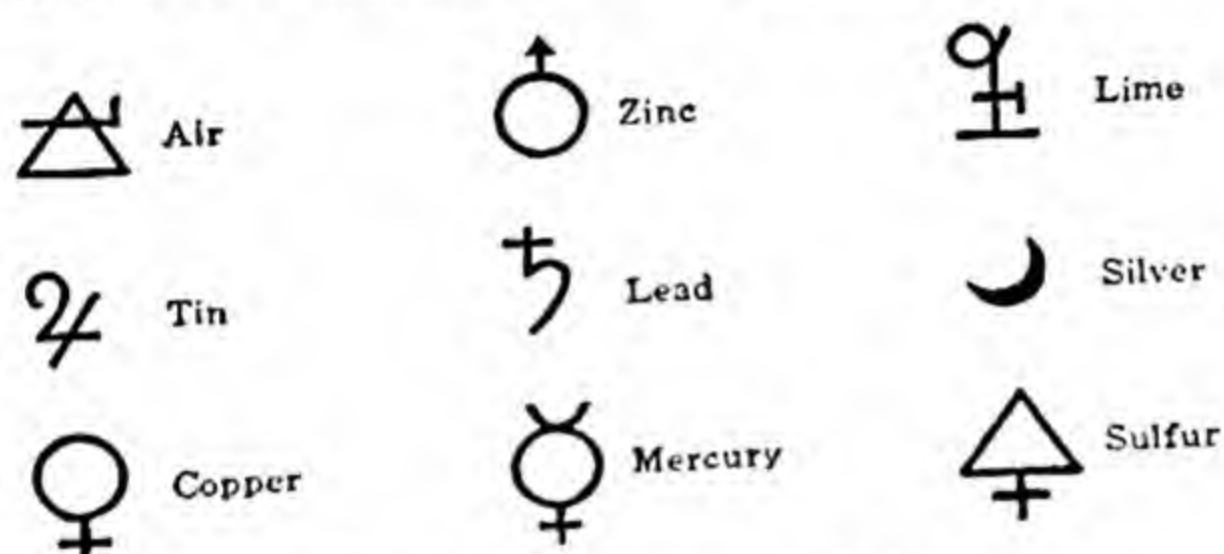


Fig. 12. Alchemists symbols.

is C, for copper Cu, for chlorine Cl, for calcium Ca, and for cobalt Co. It was fortunate that Ag (from the Latin *argentum*) was taken as the symbol for silver because S had already been selected for sulfur and Si for silicon. Fe for iron is taken from the Latin *ferrum*, Na for sodium from *natrium*, Pb for lead from *plumbum*, K for potassium from *kalium*, and W from the German *wolfram*. According to our present conception *symbols stand not only for the elements but for definite parts by weight of the elements*. For example, H represents a single atom of hydrogen and it may also mean the atomic weight in grams, that is, 1.008 grams. O means

either a single atom of oxygen or 16 g. of oxygen. A table of atomic weights is given inside the front cover.

To represent the formula of a compound we simply join the symbols of the constituent elements together and attach small sub-figures to represent the actual numbers of atoms in each molecule. H_2O as a formula for water tells us that two atoms of hydrogen and one atom of oxygen make up a single molecule of water. The weight of the whole molecule, 18.016, is of course the sum of the weights of all the atoms in it. The formula O_2 for the substance oxygen tells us that there are two oxygen atoms in each molecule with a molecular weight of $2 \times 16 = 32$. H_2SO_4 , as a formula for sulfuric acid, tells us that a molecule of the acid contains two atoms of hydrogen, one of sulfur, and four of oxygen. The formula weight is 98.082 g.

ATOMIC WEIGHTS

$$\begin{aligned}\text{H} &= 1.008 \\ \text{S} &= 32.066 \\ \text{O} &= 16\end{aligned}$$

MOLECULAR WEIGHTS

$$\begin{aligned}2 \text{ H} &= 2.016 \\ \text{S} &= 32.066 \\ 4 \text{ O} &= 64. \\ \hline \text{H}_2\text{SO}_4 &= 98.082\end{aligned}$$

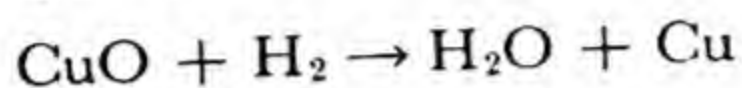
Exercise

1. The ruby (except for a trace of coloring matter) is aluminum oxide, Al_2O_3 . Explain its formula. Red lead, so common in red paints, is Pb_3O_4 , quicklime is CaO , and methane, which makes up over 90 per cent of natural gas, is CH_4 . Explain all the meanings of all these formulas.

SYMBOL-FORMULA	SUBSTANCE	AMOUNT	
H	Hydrogen	1 atom (or 1.008 g. when solving problems)	
O	Oxygen	1 atom (or 16 g. when solving problems)	
H_2O	Water	$\left\{ \begin{array}{l} 2 \text{ atoms hydrogen} \\ 1 \text{ atom oxygen} \end{array} \right.$	$\left\{ \begin{array}{l} 18.016 \text{ g. of water} \\ \text{when solving} \\ \text{problems} \end{array} \right.$
H_2SO_4	Sulfuric Acid	$\left\{ \begin{array}{l} 2 \text{ atoms hydrogen} \\ 1 \text{ atom sulfur} \\ 4 \text{ atoms oxygen} \end{array} \right.$	$\left\{ \begin{array}{l} 98.082 \text{ g. of acid} \\ \text{when solving} \\ \text{problems} \end{array} \right.$
$3 \text{ H}_2\text{O}$	Water	$\left\{ \begin{array}{l} 6 \text{ atoms hydrogen} \\ 3 \text{ atoms oxygen} \end{array} \right.$	$\left\{ \begin{array}{l} 54.048 \text{ g. of water} \\ \text{when solving} \\ \text{problems} \end{array} \right.$

The order of elements in a formula makes no difference but it is well to follow the conventions.

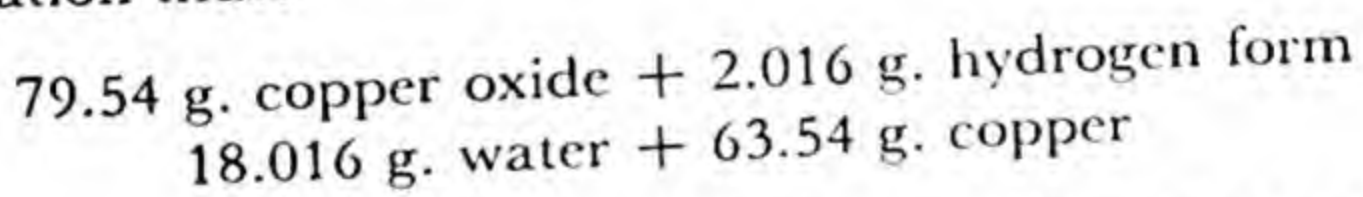
Equations. With the use of symbols and formulas we can now represent chemical changes (reactions) very simply and clearly. For example, the equation¹



tells us at least that one molecule of copper oxide reacts with one molecule of hydrogen to form one molecule of water and one atom of copper (Fig. 5, page 19). The weight of one molecule of CuO is obviously the sum of the weights of all the atoms in it. Cu = 63.54 and O = 16. Therefore CuO = 79.54. The weight of H₂ = 2.016; of H₂O = 2.016 + 16, or 18.016.

When you saw that hot H₂ steals oxygen from hot CuO, a metallic oxide, what question did you ask yourself? Of course, "Would hot H₂ steal oxygen from other hot metallic oxides?" Yes, it does, from most of them.

It is a very useful practice with problems to consider these weights as expressed in grams. Of course the relative values are just the same whether expressed in the minute units of atomic weights, or in grams or tons. Expressed in grams we should read the equation thus:



These so-called equations name the reacting substances and their products. "Balancing the equations" consists in prefixing such numbers before the molecular formulas as indicate the relative number of molecules concerned.

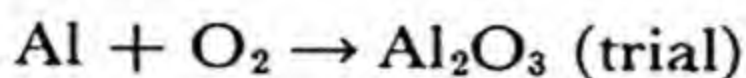
We admit that unless the student knows from his own (or some other chemist's) observations and tests in the laboratory just what the products are, it will be mere guesswork for him to attempt to balance the equation. Even when he knows the name and properties of a product, he may be ignorant of its correct formula. However, it is always possible to look up the name in the index of the text and to consult the page referred to. Repetition of such

¹ It used to be the universal custom to represent such a reaction thus: CuO + 2 H = H₂O + Cu, hence the name "equation." In reading equations aloud one usually says "form" instead of "equal."

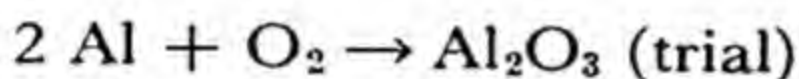
efforts and the invaluable habit of *thinking formulas* along with names will soon bring a working familiarity.

Since facility in balancing equations comes only with considerable practice, it may be well to try another example.

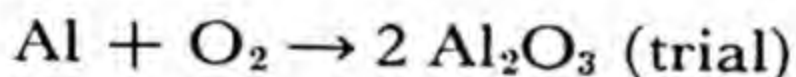
Suppose we tell you that aluminum powder, with aid of a blowtorch, can be burned in air or in oxygen gas and that the product is aluminum oxide, Al_2O_3 . The oxygen molecule is always represented as O_2 .



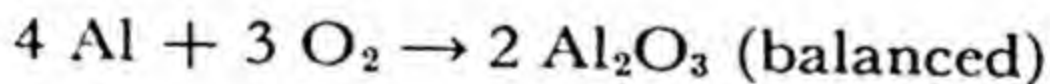
To have any aluminum oxide at all we must write down at least one molecule, that is, Al_2O_3 . This forces us to start with 2 Al on the left and also with three atoms of oxygen. It is not usual to represent 3 O as $1\frac{1}{2} \text{O}_2$, although the relative numbers of atoms could be so represented.



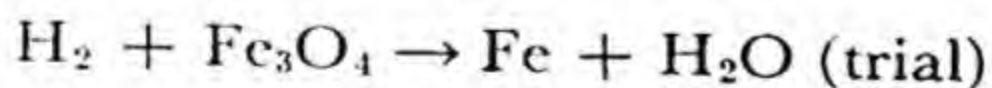
Since trial with one molecule of Al_2O_3 failed, we next try $2 \text{Al}_2\text{O}_3$. Note that the prefix 2 multiplies *all* the atoms represented by the simple formula Al_2O_3 .



This forces us to start with 4 Al and 6 atoms of oxygen (represented as 3O_2) on the left.



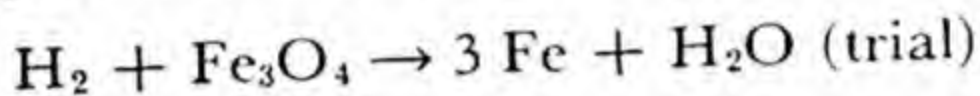
Suppose the student knows by *laboratory observation* that hydrogen reacts with hot black iron oxide to form iron and steam. He would represent this reaction tentatively by merely writing down the formulas thus:



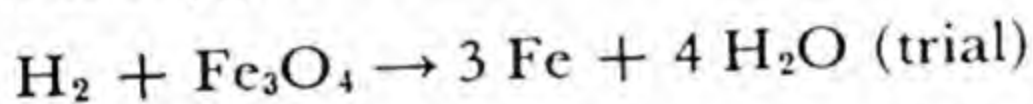
But not *all* the atoms in the reacting substances are found in the products. (Why would such an equation as it stands be a denial of the Law of Conservation of Mass?)

After all, such a reaction is merely a regrouping of the elements in new combinations, so the student must account for all the atoms. There must be an *equal* number of H atoms on both sides,

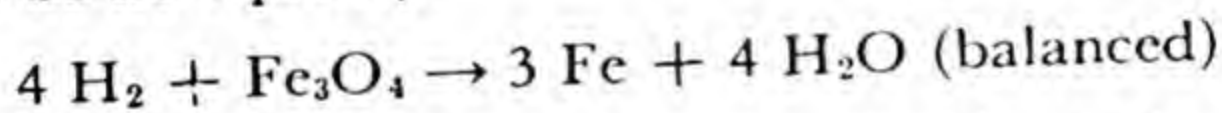
of Fe atoms, and of O atoms also. So the student begins with the most intricate formula and decides to try *one* molecule of Fe_3O_4 . He cannot use less. We do not prefix "1" to molecules; it is understood if no number is given. As a result of deciding to try balancing with *one* molecule of Fe_3O_4 , we must account for three atoms of Fe on the right-hand side of the equation. Making this change, the equation will improve:



It is evident that the four oxygen atoms in the Fe_3O_4 molecule are not all found in a single molecule of H_2O . It must require 4 H_2O to dispose of them because each molecule of H_2O uses only one atom of oxygen. So another improvement is made:



But to write 4 H_2O on the right side requires that we place eight atoms of hydrogen, found in four molecules of H_2 , on the left or there will be no equality:



Now every atom is accounted for on both sides and no violence has been done to the inner structure of any compound nor has anything been represented that was not produced in the laboratory. The equation is, therefore, properly "balanced."

(The black oxide, "hammer scale," is formed from the union of hot iron with oxygen, and the red oxide, rust, is formed at room temperatures.)

A chemical equation, then, must represent the reacting substances, the products formed and the relative weights involved. It does not, however, name the conditions — temperature, etc. — necessary to cause the reaction to take place; nor does it tell how rapidly it occurs nor to what extent the reaction occurs.

Calculation of Percentage Composition of Compounds from Formulas. If the correct formula for black iron oxide is Fe_3O_4 , it is a simple matter to calculate the percentage of iron. For example, from the formula we learn that the molecular weight is the sum of three times the atomic weight of iron (3×55.85)

plus four times the atomic weight of oxygen (4×16), or a total weight of 231.55. The iron fraction is evidently $\frac{167.55}{231.55} = 0.7236 = 72.36$ per cent of the oxide.

Determination of Formula from Analysis. Suppose analysis showed a compound to contain 27.06 per cent of sodium, 16.47 per cent of nitrogen, and 56.47 per cent of oxygen. What is the formula of the compound?

IN 100 G. OF COMPOUND	ATOMIC WEIGHTS IN GRAMS	NUMBER OF GRAM-ATOMIC WEIGHTS OF EACH ELEMENT IN 100 G. OF COMPOUND
27.06 g. sodium	Na = 23 g.	$27.06 \div 23 = 1.176$ sodium
16.47 g. nitrogen	N = 14 g.	$16.47 \div 14 = 1.176$ nitrogen
56.47 g. oxygen	O = 16 g.	$56.47 \div 16 = 3.528$ oxygen

This ratio between the number of gram-atomic weights of the three elements present, $1.176 : 1.176 : 3.528$, may be written $1 : 1 : 3$, as shown by using 1.176 as a common divisor.

Be sure to divide each "number of gram-atomic weights of each element in 100 grams of compound" by the smallest number of the three, if small whole numbers result as quotients. Otherwise select some other common divisor. Hence there are in each molecule one atom of sodium, one atom of nitrogen, and three atoms of oxygen, and the formula is NaNO_3 . Of course this ratio would hold if the molecule were two or three times as heavy, but it is best to accept the simplest formula. Later we shall learn how to determine the weight of each molecule and to apply that knowledge to the determination of formulas.

Exercises

2. A certain compound contains, by analysis, 29.40 per cent of calcium (Ca), 23.56 per cent of sulfur (S), and 47.04 per cent of oxygen. What is its formula?
3. From the percentage composition alone could you tell whether H_2SO_4 or $\text{H}_4\text{S}_2\text{O}_8$ was the correct formula for sulfuric acid?
4. Derive the formula of a compound containing 25.57 per cent magnesium and 74.43 per cent chlorine.
5. What per cent of nitrogen is found in pure lead nitrate, $\text{Pb}(\text{NO}_3)_2$?

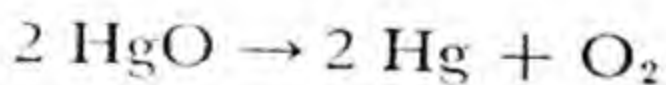
6. Write the equation for reduction of lead trioxide, Pb_2O_3 , to lead and water, by hot hydrogen. For red lead, Pb_3O_4 , by hot hydrogen.
7. Barium chloride is 65.951 per cent barium and 34.049 per cent chlorine. What is its formula?
8. A certain compound analyzes 43.394 per cent sodium, 45.285 per cent oxygen, and 11.321 per cent carbon. What is it?
9. What is the formula of a substance analyzing
 26.585 per cent potassium,
 35.390 per cent chromium, and
 38.025 per cent oxygen?
10. What is meant by the formula, $\text{C}_4\text{H}_{10}\text{O}$ (ether)? Weight of the molecule?
11. If the percentage composition of a compound is
 Ba = 58.847
 S = 13.735
 O = 27.418
 what is its formula?
12. What weight of the red iron oxide, Fe_2O_3 , may be obtained from 250 grams of oxygen and sufficient iron? What weight of the black Fe_3O_4 ?
13. On burning 0.763 g. of iron in oxygen the product weighs 0.982 g. Derive the formula.
14. How many grams of hydrogen are required to reduce 200 g. of Fe_3O_4 to the metal? 6.98 g. *Ans.*
15. In 1844 a certain chemist without reasoning power analyzed human skin and announced its formula as $\text{C}_{10}\text{H}_{66}\text{N}_{12}\text{O}_{15}$ S. What simple fact did he overlook? Could he have determined a formula for cherry pie?

Chapter 5 OXYGEN

History. The history of modern chemistry begins with the discovery of oxygen, the most important element. In 1774 Priestley, an English clergyman, heated a number of different substances in glass tubes filled with mercury and inverted in dishes of mercury. The source of heat was the sun's rays concentrated by a lens. On heating a substance later known as red mercuric oxide a gas was evolved in which a candle burned far more brilliantly than in air. Furthermore, a mouse became much more active in this gas than in air. Priestley named the gas "dephlogisticated air." It was produced from the mercuric oxide as represented by the equation



Fig. 13. Joseph Priestley.



Priestley's burning-glass was really a pair of lenses, one 16 inches and the other 7 inches in diameter, set 16 inches apart. It is now in possession of Dickinson College.

A year earlier Scheele, a brilliant chemist and drug clerk in Sweden, obtained oxygen by heating manganese dioxide. In a similar manner he prepared the gas from potassium nitrate and from five other substances. In addition to that contribution Scheele was the first to make chlorine, tungstic acid from ores, and hydrogen sulfide. He was also the first to show that lactic acid

occurs in sour milk, as well as to observe the darkening of silver salts in light. Priestley published his results first, but both men deserve credit as independent discoverers.

Priestley breathed some of this new "air" and described his sensations thus:

"I fancied that my breast felt peculiarly light and easy for some time afterwards. Who can tell but that in time this pure air may become a fashionable article of luxury? Hitherto only two mice and myself have had the privilege of breathing it."

Oxygen has not become a luxury but a blessing to humans in extreme exhaustion and illness, and a rescuing aid above and below land and sea.

Lavoisier, a celebrated Frenchman, sometimes called the "father of modern chemistry," at once applied himself to a systematic study of the new substance, and by a convincing experiment showed its relation to air and to the process of combustion.

He heated mercury in a retort over a charcoal fire (Fig. 15) for twelve days, until there was no further change, and then observed a red powder formed on the surface of the mercury. The end of the retort dipped under a jar in a larger dish of water, so the volume of the air in the retort and the jar was definitely known. During the heating this *volume decreased one-fifth* and the gas left in the retort extinguished a burning splinter. When the red powder was heated to a still higher temperature as in Priestley's experiment a volume of gas was given off *exactly equal to the loss in volume of the original air*. Moreover this evolved gas possessed all the properties of Priestley's "dephlogisticated air." Lavoisier named it "oxygen" from the Greek word for "acid-producer," because he thought it was contained in all acids. In this he was mistaken, but he was right in his conclusion that oxygen is an essential part of air.

Lavoisier's experiment cleared up the current uncertain ideas of combustion and rusting, for he had calcined or rusted mercury,



Fig. 14. Priestley's double lens which he used to concentrate the sun's heat on mercuric oxide. Now to be seen at Dickinson College.

showing that it united with oxygen from the air to form an ash, mercuric oxide. The revolutionaries guillotined Lavoisier in 1794.

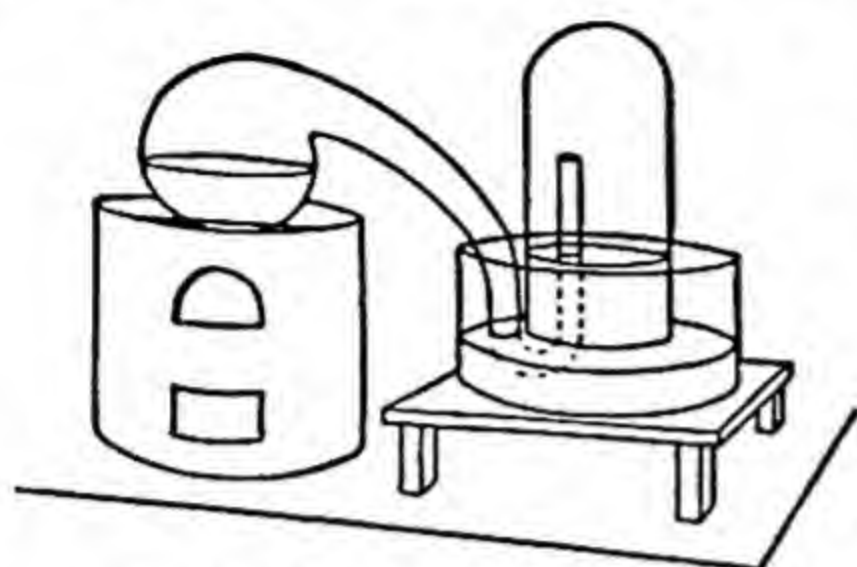


Fig. 15. Lavoisier's experiment.

Experiments somewhat similar to Lavoisier's were carried out by the Russian Lomonossov in 1756, using tin powder instead of mercury.

Prior to Lavoisier's experiment substances were supposed to lose a mysterious spirit, called "phlogiston," in the process of burning.

Exercise

1. From some good history of chemistry learn other incidents in the lives of Priestley and of Lavoisier.

Occurrence. Oxygen makes up one-half of all matter that we know. Two-thirds of the human body is combined oxygen. Water contains 89 per cent; ordinary clay, sand, limestone, and granite about 50 per cent. One-fifth of the air is free oxygen, the other four-fifths nitrogen and other gases. This is the only occurrence of free oxygen except the little that is found dissolved in water. Elsewhere it is found in compounds.

Preparation. There are at least four general methods of preparation of oxygen, but its most important commercial source is the atmosphere. Air is chiefly a mixture of oxygen and nitrogen but separation is not easy.

INDUSTRIAL METHODS

1. Air Liquefaction Process — the leading process
2. Electrolytic Method

1. The separation of oxygen from the nitrogen with which it is mixed in air is accomplished by *liquefying air* and then allowing it to evaporate. The more volatile nitrogen escapes first, leaving the oxygen, which is usually stored in strong steel cylinders at 100 atmospheres pressure.

One ton of coal has furnished the energy required to separate one ton of oxygen from four tons of nitrogen by the liquefaction process but much greater efficiency is promised.

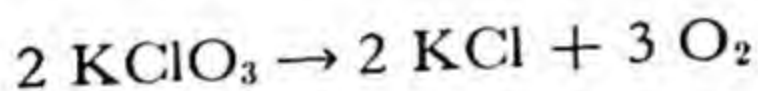
2. The *electrolysis of water* (decomposition by passage of an electric current) releases hydrogen at the cathode (negative) and oxygen at the anode (positive) if an acid or base is present to make the water conduct electricity.

3. The laboratory methods, where convenience is more important than cheapness, in most cases consist in *heating oxygen compounds*.

LABORATORY METHODS

3. Thermal Decomposition of Oxygen Compounds
4. Sodium Peroxide Method

Potassium chlorate melts at 351°C . and at about 400°C . releases oxygen:¹



If into a test tube partly filled with melted potassium chlorate which is giving off very little oxygen we drop a mere pinch of powdered manganese dioxide, there is at once an enormous increase in the rate of evolution of the gas. Potassium chlorate alone does not give off oxygen much below 400°C ., yet in the presence of manganese dioxide the gas is rapidly released at 200°C . This is the basis of the usual laboratory method. No exact amount of manganese dioxide is needed. About one-fourth as much as the weight of the potassium chlorate is satisfactory. The manganese dioxide aids the reaction and is called a "catalyst"

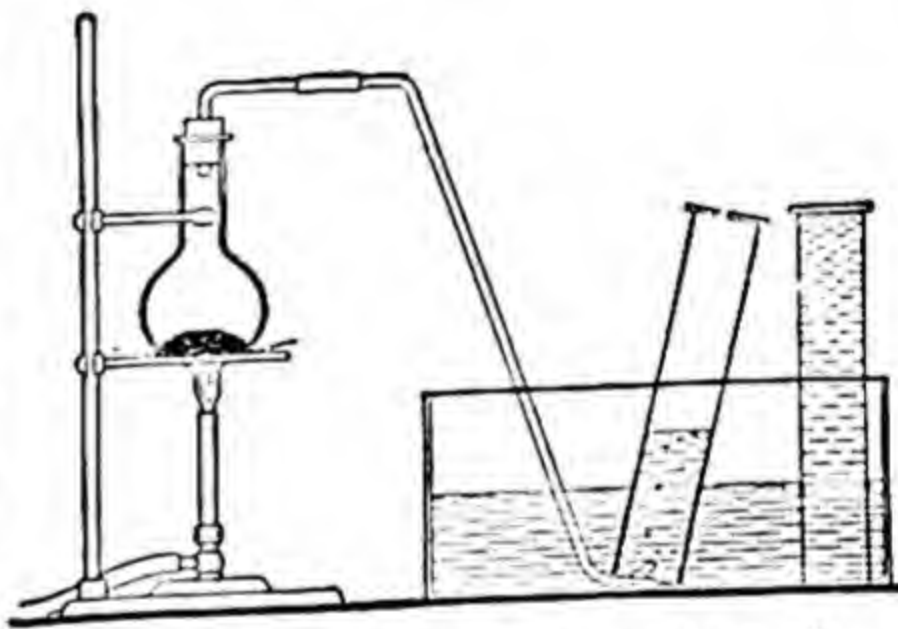
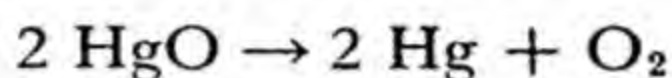


Fig. 16. Laboratory preparation of oxygen.

¹ In reality, potassium perchlorate, KClO_4 , is first formed and this at higher temperatures gives up all its oxygen.

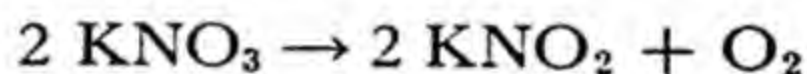
(see page 53). In Fig. 16 is represented the usual laboratory method of preparing oxygen in quantity. The oxygen evolved from the heated mixture of potassium chlorate and manganese dioxide is collected by displacement of water, in which it is but slightly soluble. Iron oxide, Fe_2O_3 , is even more efficient than manganese dioxide while chromium trioxide, Cr_2O_3 , is the best of all catalysts. Potassium chlorate should never be heated in contact with combustible material. Danger! Neither should sodium peroxide come in contact with such material when moist.

Like Priestley we may heat mercuric oxide:



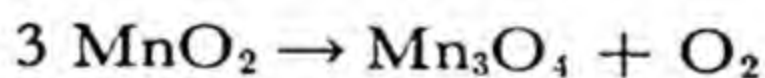
The mercury is volatilized and condenses as a mirror or in drops on the cooler parts of the tube. Oxides of gold and silver are also readily decomposed.

We may emulate Scheele and heat potassium nitrate:

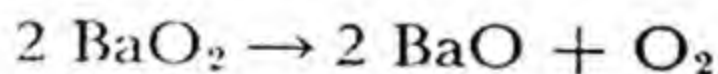


A third of the oxygen escapes and potassium nitrite remains.

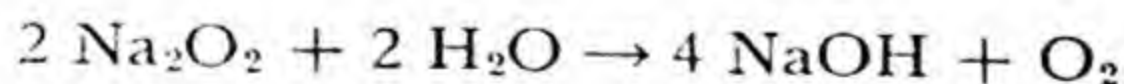
Manganese dioxide when heated very hot gives off only part of its oxygen:



Barium dioxide, better called barium peroxide, releases just half its oxygen when sufficiently heated:



4. *Sodium peroxide* (made by heating sodium in air) reacts rather violently with water to form oxygen and sodium hydroxide:



This is expensive but very convenient, because the water may be allowed to drop slowly from a dropping funnel on the peroxide, releasing oxygen as needed.

Physical Properties. Oxygen is a colorless, odorless, tasteless gas which is 1.105 times as heavy as air. One liter weighs 1.429 g. measured at 0°C . and a barometric pressure of 760 mm. It may

be liquefied at and below -118°C ., but no pressure is great enough to compress it to a liquid above -118°C ., which may therefore be called its *critical temperature*. Under less pressure it remains a gas. At the critical temperature 50 atmospheres pressure are required to liquefy oxygen; hence this is the *critical pressure*. Of course at temperatures below -118°C . a lower pressure than 50 atmospheres can cause liquefaction.

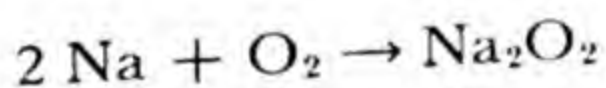
Liquid oxygen is light blue in color and boils at -182.5°C . under atmospheric pressure. It is attracted to a magnet, but far less strongly than is a bar of iron. Dewar froze oxygen to a pale blue, snowlike solid, melting at -218.4°C .

Oxygen is slightly soluble in water. At 20°C . and 760 mm. pressure 100 ml. of water dissolve 3 ml. of oxygen (0.004 g.). Oxygen is 8.6 times as soluble in alcohol as in water (at 760 mm. pressure). Curiously enough it dissolves in molten silver, 10 ml. in 100 ml. of the silver, but is released on cooling.

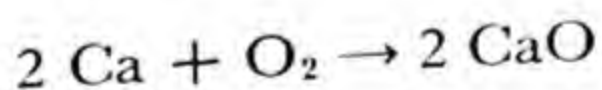
Liquid oxygen may be shipped or stored for several days in huge thermos bottles (Dewar bulbs).

Chemical Properties. Oxygen is only moderately active chemically at ordinary temperatures, but at elevated temperatures it unites with nearly every element. It is true that sodium rapidly oxidizes at room temperature but iron rusts slowly and carbon is attacked very slightly indeed unless heated.

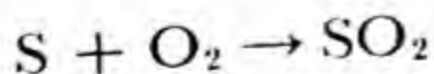
If the metal sodium is heated and then placed in a jar of oxygen, it burns brilliantly with a yellow flame. The only possible reaction is the direct combination of the two elements forming a sodium oxide or, under these conditions, sodium peroxide:



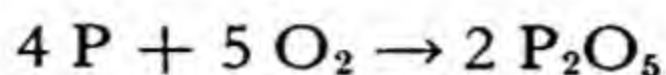
Calcium burns almost as brilliantly, forming ordinary quicklime or calcium oxide:



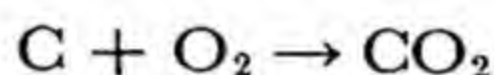
Sulfur, first ignited with a flame, also burns with far greater vigor in oxygen than in air, forming sulfur dioxide:



Red phosphorus burns with a dazzling flame and the formation of a dense white smoke of phosphorus pentoxide:



The experiment with carbon is best performed with a stick of charcoal, which can be held in the forceps. After igniting it in the Bunsen flame, it is thrust into a jar of oxygen, where, instead of merely glowing, it bursts into flame. Pure carbon burns with a pale blue flame:



It seems incredible, but iron in the form of steel wool or picture wire will burn in oxygen if first heated red hot. It may be necessary to dip the end of the wire into sulfur as a sort of match head. Dazzling sparks (Fig. 17) fly in all directions, and drops of molten iron often break the glass bottles. Water in the jar may prevent the breakage.



After these oxides have been formed, a little pure water is added to each jar, which is then closed and shaken.

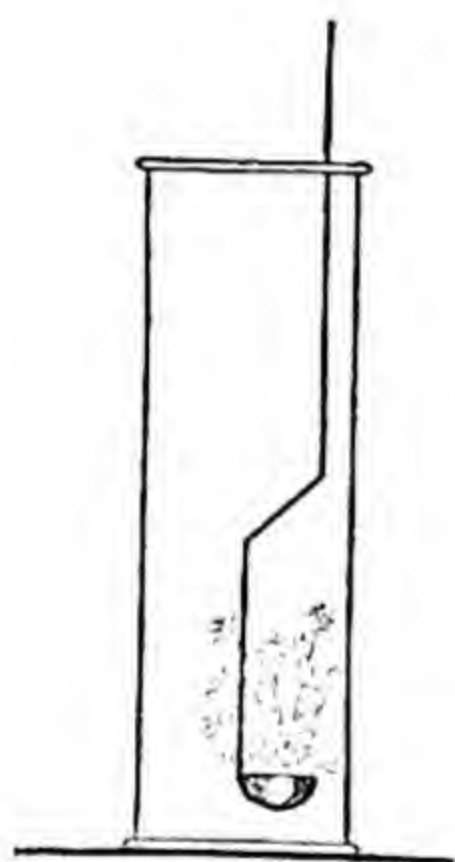
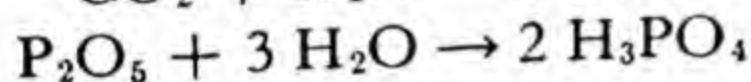
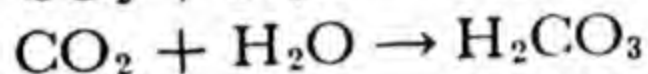
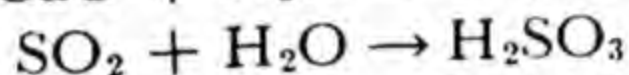
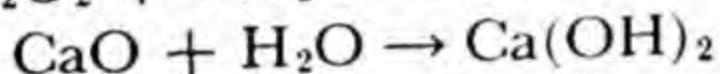
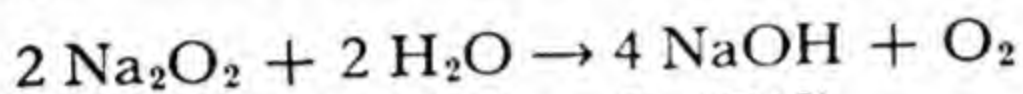


Fig. 17. Burning steel wire in oxygen.

It may be noted here that black Fe_3O_4 is always the product formed by high-temperature oxidation of iron while red Fe_2O_3 is the product of ordinary rusting.

A small piece of blue litmus paper and one of red are dropped into each jar. The water with the sodium oxide turns red litmus blue, as does the calcium oxide water. Both waters feel soapy to the touch. The sulfur dioxide water turns blue litmus red as does the carbon dioxide water. The effect of the iron oxide water is too slight to be detected. These oxides have reacted with water in two ways, some to form *bases* which turn red litmus blue and some to form *acids* which turn blue litmus red. Elements whose oxides react with water to form bases are called *metals* and ele-

ments whose oxides react with water to form acids are called *non-metals*. (These oxides are known as the *anhydrides* of bases and of acids although the term is generally used for acids only. It is implied that subtraction of H_2O from the formula of an oxygen acid must give us the formula of its anhydride. For example, H_2SO_4 less $\text{H}_2\text{O} = \text{SO}_3$ and 2HNO_3 less $\text{H}_2\text{O} = \text{N}_2\text{O}_5$.)

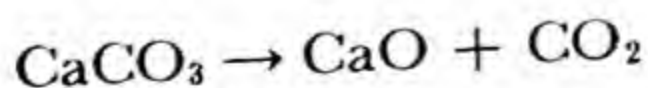


The products above are called sodium hydroxide, calcium hydroxide, sulfurous acid, carbonic acid, and phosphoric acid, respectively. The definition of *acids* will be given later, but we know them as sour substances that in water solution turn litmus red, attack some metals, and neutralize the properties of bases. We know *bases* as substances that in water solution feel soapy, turn litmus blue, and neutralize the properties of acids.

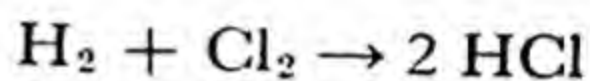
Metals (iron, copper, gold, nickel, and lead, for example) show such physical properties as good conductivity for heat and electricity, malleability, ductility, and luster. Non-metals (sulfur, carbon, chlorine, arsenic, and nitrogen, for example) in general do not exhibit these properties.

These are only convenient general statements for there are a number of border-line elements.

Oxides. An oxide is a compound of oxygen with one other element. Water is an oxide of hydrogen. Potassium chlorate is not an oxide, for it contains more than two elements. Most oxides can be made by direct combination of oxygen with one other element, but a few elements like gold and platinum must be led into such union by indirect methods. Many oxides are made conveniently by heating carbonates, nitrates, or hydroxides. As an example may be noted the heating of limestone to yield quicklime:



Combustion. When substances react heat is usually (but not always) liberated. If the reaction becomes so vigorous that light is also produced, it is called combustion. As a rule this term is applied to a union of oxygen with other substances, but many other reactions produce light. The burning of fuel in a furnace is a common example of combustion. Sodium and magnesium burn almost as brilliantly in carbon dioxide gas as in air, forming oxides and free carbon in each case. A jet of chlorine gas burns with a flame in an atmosphere of hydrogen gas; also, a jet of hydrogen burns in an atmosphere of chlorine:



Phlogiston. Becker, and later Stahl (1723), sought to explain combustion by assuming the escape of a sort of volatile spirit called phlogiston! The ash of wood no longer burned because it had lost all of its phlogiston.

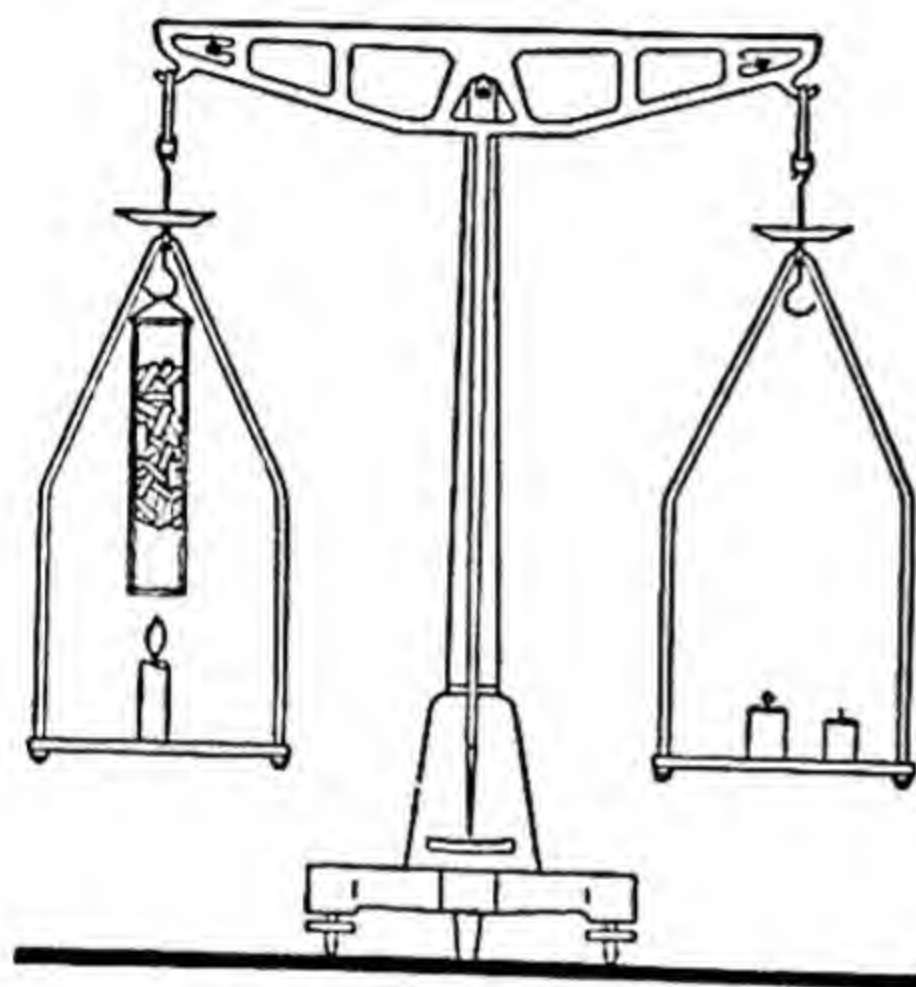


Fig. 18. Weighing all the products of combustion.

2. Why does the ash of wood or coal weigh less than the original fuel while the ash of heated metals weighs more?

In Fig. 18 is represented a candle placed directly under an open tube filled with sticks of sodium hydroxide, all balanced by weights on the other pan of the balance. When the candle is lighted the pan on the left sinks. The increase in weight is due to the fact that oxygen of the air unites with the volatilized wax of the candle and to the additional fact that the gaseous products of combustion are caught by the sodium hydroxide.

A magnet holding iron filings may be hung from the left end of the balance, and counterpoised by weights on the pan on the right. If, now, the magnet and filings are heated with a gas flame the formation of an iron oxide is indicated by the increase in weight.

Heat of Combustion. Reactions accompanied by the evolution of heat are *exothermic*, and those that require the application of external heat to sustain them are *endothermic*. In measuring heat

we use the calorie as a unit. A *calorie* is the amount of heat required to raise the temperature of one gram of water one degree (at 15° C.). The large calorie (Cal.), one thousand times as great, is sometimes called the kilogram calorie. The heat of combustion of a substance may be determined with a calorimeter bomb

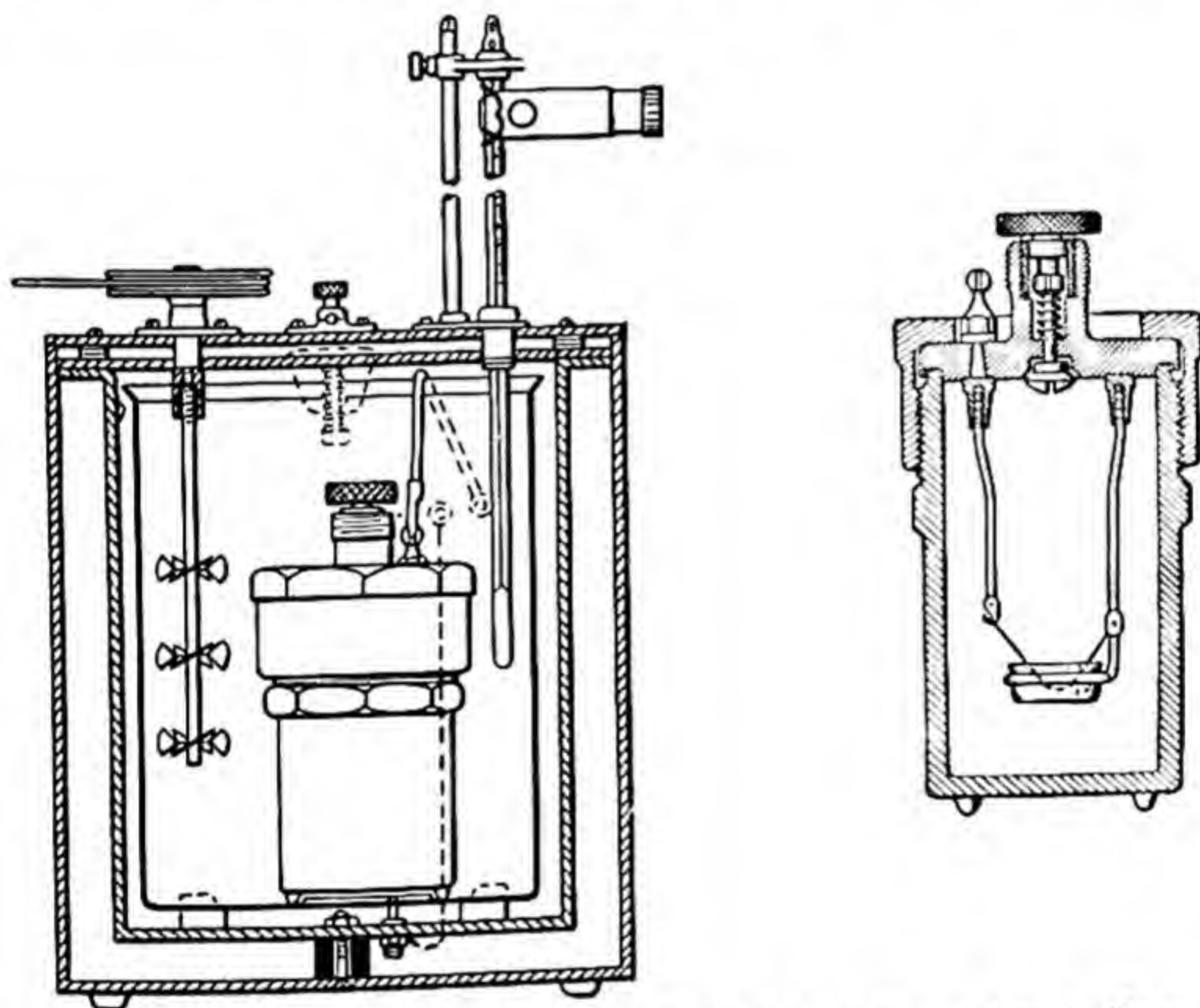


Fig. 19. Heat of combustion determined with a calorimeter bomb (Parr type) immersed in a known weight of water. Thermometer and stirrer are shown at left. At right is the bomb alone with electric ignition device to start combustion of sample in compressed oxygen. (Welch Scientific Co.)

(Parr type) immersed in a known weight of water with a thermometer and stirrer. The bomb, with an electric ignition device to start combustion of the sample in compressed oxygen, is shown in the center of Fig. 19.

The *heat of combustion* of any pure substance is the number of calories liberated when a formula weight (molecular weight in grams) is burned. For example, a molecule of carbon monoxide weighs 28, hence its formula weight is 28 g. When 28 g. of this gas burns, it liberates 68,400 calories and becomes carbon dioxide

Of course the heat of combustion of hydrogen is the same as the heat of formation of water. It is also obvious that substances with the highest heat of formation must be the hardest to decompose by application of external energy. The amount of heat required to decompose a given weight of a compound into its constituents is equal to the amount of heat given off when the same weight of the compound is formed from its elements.

The following table gives the heat of combustion of several substances:

SUBSTANCE	FORMULA WEIGHT	HEAT OF COMBUSTION
Carbon	C = 12 g.	94,480 calories
Sulfur	S = 32 g.	70,920
Hydrogen	H ₂ = 2 g.	68,310
Carbon monoxide	CO = 28 g.	68,400
Methane	CH ₄ = 16 g.	210,800

3. How much heat is liberated when 58 g. of sulfur burn? When 120 g. of carbon burn to CO₂?

In the auto, 1 gal. gasoline + 1200 cu. ft. air → Exhaust gases
 (including nitrogen) $\left\{ \begin{array}{l} 7 \text{ lbs. water} \\ 12 \text{ lbs. carbon} \\ \text{dioxide} \\ 4 \text{ lbs. carbon} \\ \text{monoxide} \end{array} \right.$

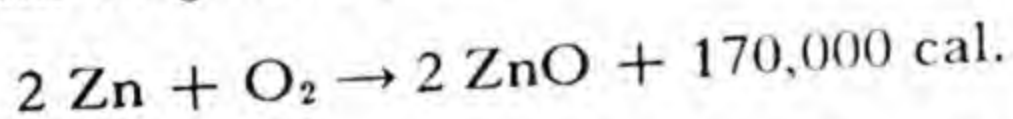
Engineers quite commonly refer to British Thermal Units, B. T. U., instead of calories. This B. T. U. is the amount of heat required to raise the temperature of one pound of water 1° F. Since 1 pound = 453 g. and 1° F. = $\frac{5}{9}$ of 1° C., it is evident that 1 B. T. U. = 252 calories. Very good soft coal may yield 15,000 B. T. U. per pound of dry fuel.

4. A ton of coal with a B. T. U. value of 15,400 per pound will raise the temperature of how many liters of water 70° C.?
5. Calculate the number of B. T. U. obtained by burning 12 pounds of sulfur. The heat of combustion of sulfur is 70,920 calories.

An exothermic reaction frequently continues of its own accord when once started, but an endothermic reaction continues only when forced to do so by the use of energy from external sources.

Chapter 6 OXYGEN (continued), AND OZONE

Oxidation. The union of oxygen with a substance is called oxidation. (Later we shall find other reactions also included under that term in a broader definition.) Oxidation may be so slow that no light is evolved and very little, if any, rise in temperature noticed. As a matter of fact when a gram of any substance is oxidized slowly, exactly the same quantity of heat is liberated as during violent burning. In slow oxidation heat is usually conducted away so rapidly that a rise in temperature is not noticed. The rusting (slow oxidation) and the burning of metals (rapid oxidation) are both illustrated by the following equation, representing formula weights in grams:



The change from "hard" cider to vinegar is brought about by the union of alcohol of the cider with oxygen of the air to form acetic acid. The "mother of vinegar" is an organism that aids this reaction.

The animal body is a wonderful apparatus for the oxidation of food. The oxygen of the air meets the blood in the lungs and combines with the bluish hemoglobin of venous blood to form red oxyhemoglobin of arterial blood. This oxyhemoglobin is taken through the smallest capillaries and gives its oxygen to the wornout tissues of the body, burning them into carbon dioxide and water for the greater part. Carbon dioxide is exhaled from the lungs. The heat of this oxidation maintains the animal temperature and is approximately equal to the heat evolved when

the same food is burned rapidly in a calorimeter. In other words, the animal's body is both furnace and engine for the conversion of the chemical energy of food into heat and motion.

The "drying" of paint is not the loss of water but the oxidation of linseed oil to form a tough solid that is no longer sticky.

Finely divided lead ignites when dusted into the atmosphere.

The lead is prepared by using lead tartrate as a source of lead. This compound is obtained as a white precipitate by adding a saturated solution of rochelle salts to a saturated solution of lead acetate. The precipitate should be washed and dried. Place the lead tartrate in a 6-inch test tube to about one-third of its volume. Clamp the test tube in a horizontal position. Heat it gently with a burner and keep the temperature low by moving the flame back and forth. When the white lead tartrate has all decomposed into the black finely divided lead, stop the heating and seal the end of the tube with a paraffin dipped cork stopper. To ignite the lead, remove the stopper and allow the loose powder to drop through the air. If the tartrate is heated too vigorously the lead will not ignite when thrown into the air. (E. T. Mitchell.)

Spontaneous Combustion. If the heat from a slow oxidation is not conducted away fast enough by air currents, it may accumulate, finally bringing the temperature of the substance to the ignition point. This is *spontaneous combustion*. Coal is oxidized on storing and a loss of several per cent occurs. In rare instances the coal may ignite spontaneously. Oxidation of fat-soaked rags has been known to raise their temperature to the ignition point.

Uses of Oxygen. Oxygen is a most useful element. Essential to animal life in burning out waste tissue and furnishing heat, beneficent in its disposal of sewage and other waste matters that would otherwise be a nuisance and a menace to health, vital in developing heat, light, and power from fuel — it is, in short, the central element. Oxygen, compressed in steel cylinders, is used for the oxyhydrogen (or oxyacetylene) torch. This is a burner by which hydrogen or acetylene is burned in pure oxygen instead of in air. The extremely hot flame produced cuts through iron (by melting and burning the iron) like a knife. The transportation of scrap iron occurring in such inconvenient forms as bridges, boilers, etc., is tremendously aided by cutting it into smaller sections with the oxyacetylene torch. Again, the localized high temperatures are convenient in welding. Unfortunately the oxy-

acetylene flame has been of great help to burglars in opening safes.

The oxygen tent or mask has helped many invalids too weak to breathe the requisite amount of air. One-fifth the effort supplies the sufferer with the same amount of oxygen if the pure gas is used. In the thin air of the stratosphere aviators need the aid of cylinders of compressed oxygen and motors need the aid of superchargers.

See No. 7474

For very high altitude flying full oxygen cylinders are as important as full gasoline tanks. Each member of the crew may breathe seven cubic feet an hour. Submarine crews likewise require cylinders of compressed oxygen. As a military necessity the size and weight of the compression — cooling — distillation units for separating oxygen from air was considerably reduced. Reminiscent of the old and obsolete Brin process was research on an organic compound of cobalt that would readily take up oxygen from air and give it off (pure) at higher temperatures or lower pressures. If industrial oxygen, even of only 90 per cent concentration, can be prepared at low cost so that it can profitably be used to enrich air for the "blast" in separation of iron from its ores it would find greatly increased use. Here is a problem of great importance. Vigorous research in this field goes on, with predictions of a price drop from \$70.00 per ton to near \$3.00.

At a new plant in Texas oxygen (not air) is used for the partial oxidation of natural gas as a step in the production of gasoline and diesel fuel. Similar reaction with coal promises to result in manufacture of useful liquid fuels. Oxygen plants now under construction or planned will produce thousands of tons daily of approximately 90 per cent concentration.

Some of the German rocket bombs were probably propelled by alcohol or gasoline, and liquefied oxygen.

Influencing the Speed of Reaction. The speed of chemical reactions is greatly influenced by *temperature*, by the *concentration* of the reacting substances, by the presence of *catalysts*, and by the amount of *contact surface*.

A rise in temperature of 10°C . doubles or trebles the speed of most reactions. A rise from 20°C . to 200°C . means a millionfold

increase in velocity of reaction. This is understood when we remember that a rise in temperature means that the molecules move faster, consequently hit each other harder and oftener. Reactions probably continue at low temperatures but at rates too slow to observe. A reaction requiring 1 sec. for completion at 200°C . will require 11 days at 0°C .

Admiral Byrd found that he could not use flashlights in the south polar regions because the intense cold stopped the necessary chemical action of the dry batteries.

This temperature influence is familiar in cooking. In a pressure cooker with the steam retained by a tight lid tough meat is made tender at perhaps 125°C . in a fraction of the time required in an open vessel where the temperature would be little more than 100°C .

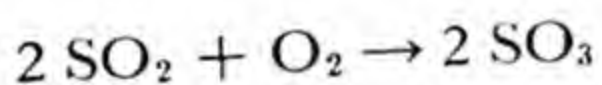
The concentrations of two substances thoroughly mixed also affect speed of reaction. The effect can be expressed quite simply in the phrase "opportunities for contact." If, for example, in a milliliter there are one million molecules of A and one million of B, the reaction takes place at a definite speed. Now if the concentration of A be doubled, two million molecules in the milliliter, it is obvious that the opportunities for contact between A and B will be doubled, that is, the speed of reaction will be doubled. If, next, the concentration of B increase to three million molecules for each milliliter, the velocity of reaction must increase to 3×2 or 6 times the original. Charcoal and other combustibles burn more brilliantly in pure oxygen than in air because only one-fifth of air is oxygen, and consequently pure oxygen at the same pressure has five times the *effective* concentration of air. Furthermore, much of the heat produced is absorbed in raising the temperature of the useless nitrogen.

With two substances that cannot be mixed thoroughly, such as a solid and a gas, the amount of surface of the solid is of great importance. Splinters or shavings burn much faster than a thick log — a matter of "opportunities for contact." Coal dust now is blown into cement kilns with air and burned like a spray of oil. It is also used in power plants.

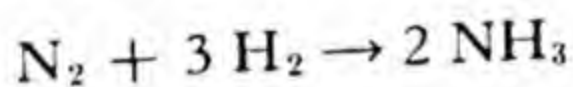
Dust Explosions. Danger from inflammable dusts occurs in industries handling flour, starch, grain, sulfur, coal, leather, alfalfa, sugar, soap, cocoa, fertilizer, feeds — in short, where any combustible material is ground into dry dust. In some years dust explosions have caused a loss of scores of lives and millions of dollars in property.

Catalysis. A *catalyst* (page 41) is a substance that aids or retards a reaction without itself being permanently changed. Some catalysts condense the reacting substances on their surface, thus bringing in the influence of increased concentration and possibly making the condensed molecules more active by weakening the attraction between the constituent atoms. In some cigar lighters the vapors of methyl alcohol mixed with air pass over a thin roughened platinum wire. There is little oxidation without the platinum. Some gas lighters act in the same way.

Other catalysts may enter into a reaction but are released in their original form by further reactions. It is evident that very small amounts of the catalysts can be used many times over, almost indefinitely, in fact. Platinum powder is an invaluable commercial catalyst, for by its aid sulfur dioxide is rapidly oxidized:



The trioxide formed finally reacts with water to form sulfuric acid. Also nitrogen and hydrogen unite at a profitable rate with the help of special catalysts:



Since ammonia (NH_3) is valuable in making fertilizers and is easily oxidized to nitric acid by the further use of platinum as a catalyst, it is plain that catalysis is not a theoretical subject.

There are thousands of catalysts, including water itself, for certain reactions.

The activity of a catalyst may be greatly affected by impurities. Increase in activity is due to "promoters" and decrease to "poisons." Pure copper catalyzes the addition of hydrogen to isopentene at 225°C ., whereas addition of only 0.1 per cent of chromium oxide to the copper catalyzes this reaction just as well at 75°C .

OZONE

Occurrence. There has been much argument as to the existence of traces of ozone in the air. In high-barometer areas, which are merely whirling mountains of air, the upper air is thrown to the earth's surface faster than under any other conditions, especially on cold, bracing days of winter. As a result the ozone formed several miles up by the ultra-violet rays of the sun reaches the surface before it is all destroyed by heat, dust, and other agencies. Air is not very permeable to ultra-violet light and so the action of these rays from the sun is greatest in the upper layers. Cold, dry, and dustfree, the upper air favors the existence of ozone.

There is evidence of the existence of an ozone blanket 25 miles above the earth, only enough to form a two-millimeter layer if pure, yet this blanket helps to protect us from sunstroke.

Properties. Ozone is a gas 1.5 times as heavy as oxygen, colorless, of a pungent odor, somewhat soluble in water and far more active chemically than oxygen. Liquefied, it is a dark indigo blue.

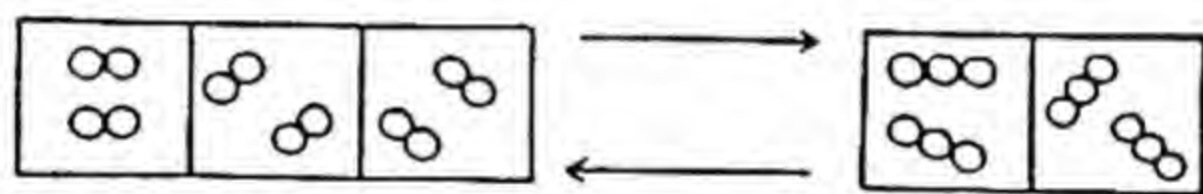
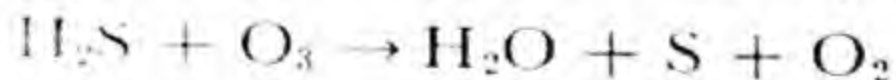


Fig. 20. Three volumes of oxygen yield two volumes of ozone.

The change from oxygen to ozone is reversible:



When ozone oxidizes any substance, it often does so with one of its three atoms, releasing a molecule of oxygen. Thus:



Ozone is more active than oxygen; it contains more chemical energy transformed from the energy of the silent electric discharge or of ultra-violet light. A gram of carbon burned in ozone thus releases more heat than a gram of carbon burned in oxygen. This additional heat comes from the decomposition of ozone.

Turpentine reacts with ozone to form an ozonide, a powerful oxidizing agent.

Preparation. Although made in nature chiefly by the ultra-violet rays of the sun, ozone is produced in the laboratory and on a commercial scale by the silent electric discharge through air or oxygen.

The irritating effects of ozone made by electric spark discharges are due to the considerable amounts of oxides of nitrogen formed along with the ozone. Ultra-violet rays yield a much better product with only a small fraction of the usual amount of toxic oxides of nitrogen.

Allotropic Forms of Elements. A number of elements such as oxygen, hydrogen, nitrogen, phosphorus, sulfur, carbon, and iron are capable of existing in two

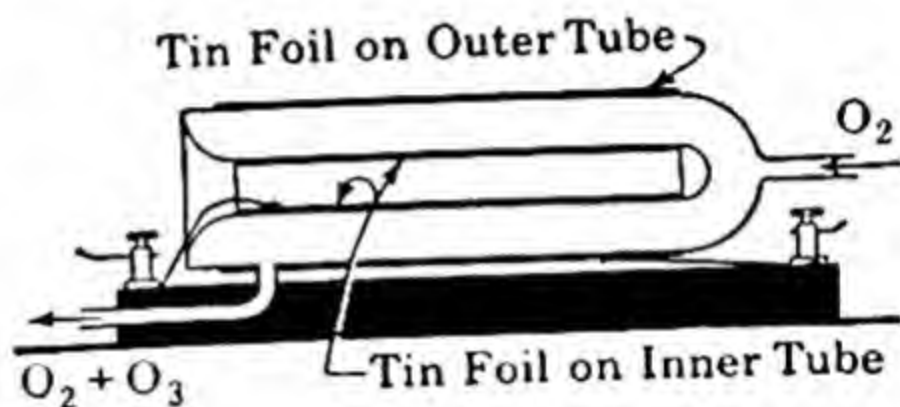
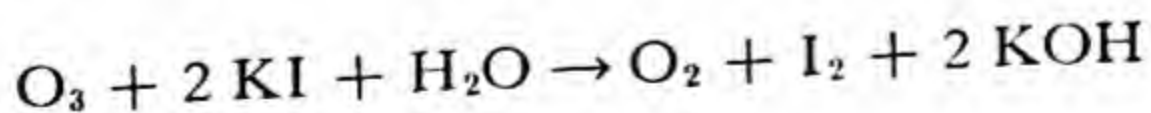


Fig. 21. Laboratory ozonizer.

or more forms, with different energy contents and different physical properties but with unchanged (or little changed) chemical properties. These *allotropic modifications* (oxygen-ozone; white phosphorus-red phosphorus; etc.) of elements are made up of molecules containing different numbers of the same atoms, or with different arrangements of atoms, and have different amounts of energy.

Uses. Ozone has been used to sterilize water, to destroy odors, to purify indoor air, to sterilize bandages in hospitals, to bleach oils, flour, delicate fabrics, and in a few oxidation processes in chemical manufacture. It is easy to overstate its value in the purification of air. Ozone is used also as a bleaching agent, a deodorizer (by oxidation of odorous substances) and as an agent for rapid oxidation of oils used in linoleum. It also has some value as an aid to oxidation by oxygen.

Tests. Some authorities claim to smell one part of ozone in 10,000,000 parts of air, rivaling hunting dogs in keenness. A simple test is the development of blue color in a starch-potassium iodide paper:

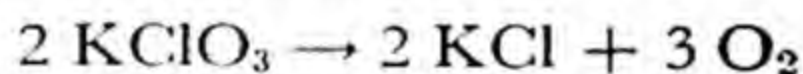


Ozone releases free iodine, which then turns blue on contact with starch. Unfortunately any good oxidizing agent such as nitric acid or hydrogen peroxide will do this. Consequently this test is useful only in their absence.

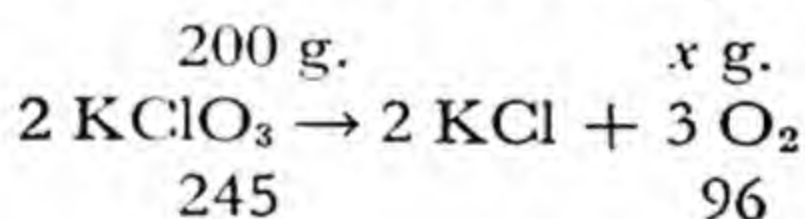
An excellent qualitative and quantitative test for ozone is described in the *Journal of Chemical Education*, 6, 1350 (1929), and in the *Analyst*, 54, 189 (1929).

The rapid weakening of rubber by ozone has been utilized in the development of a simple ozone test. (*Chemical Industry*, 49, 170 T (1930).)

Chemical Problems. If it is desired, for example, to learn how many grams of oxygen are driven off on heating 200 grams of potassium chlorate, it is a matter of simple calculation after writing the balanced equation:



Write the weights in grams of the two substances directly concerned above their formulas in the equation and the weights of the correct number of molecules or atoms just below:



Then follows $\frac{200}{245} = \frac{x}{96}$

$$x = \text{grams of oxygen released}$$

Note that we do not always set down the mere molecular weight. In the illustration above the balanced equation tells us the absolutely necessary fact that for every two molecules of potassium chlorate heated we secure three molecules of oxygen gas. We therefore compare the weights (made up of weights of all the atoms in the molecules) of 2 KClO₃ and 3 O₂.

If preferred the ratios may be written:

$$\frac{200 \text{ g.}}{x \text{ g.}} = \frac{245}{96}$$

Choose one method and stick to it.

Exercises

1. Compare the properties of oxygen and ozone.
2. Describe four methods of making oxygen.
3. Give two examples of an exothermic reaction.
4. What is catalysis? Examples?
5. Of what importance is it to fish that oxygen is slightly soluble in water?
6. How did Lavoisier prove that oxygen is one-fifth of air by volume?
7. Burn 200 g. of magnesium (flashlight metal). Does the ash weigh more or less than 200 g.? How about a candle?
8. Why select oxygen as the first element to study?
9. What weight of oxygen may be obtained by heating 480 g. of barium peroxide?
10. What percentage by weight of free oxygen is obtained by heating (1) mercuric oxide, (2) barium peroxide, (3) potassium chlorate? At \$1.50, \$1.00 and \$0.15 per kg. respectively, which is the cheapest source of oxygen?
11. How many grams of oxygen will be obtained by treating 149 g. of sodium peroxide with excess water?
12. Complete these statements: Phosphorus pentoxide is the . . . of phosphoric acid. Calcium oxide reacts with . . . to form the base, calcium hydroxide.
13. Why do you suppose Lavoisier stopped heating the mercury at the end of twelve days and why didn't he quit at the end of a week?
14. How can reactions be speeded up? Between a solid and a gas? A solid and a liquid?
15. What makes ozone in the upper air?
16. If 68,310 cal. of heat are released when 2.016 g. of hydrogen unite with 16 g. of oxygen to form 18.016 g. of water, how much heat (or its equivalent in electricity) would be required to decompose 18.016 g. of water?
17. Which of the following will be the most stable? Which the least? Heats of formation are given below.

Zinc oxide	85,000 cal.	Silver oxide	6,950 cal.
Magnesium oxide	146,100 cal.	Silicon dioxide	201,400 cal.
Aluminum oxide	399,000 cal.		
18. While we were grinding pure potassium chlorate in a clean mortar in our laboratory a sharp explosion occurred. We observed that the pestle had a handle of wood and a grinding end of porcelain. Can you explain the explosion?
19. Why not attempt to burn the ashes from your furnace again, and again? We assume efficiency in the fireman.

20. If oxygen suddenly became very soluble in water what changes in life on earth would take place?
21. Priestley was the first to collect gases over mercury. What type of gases do you think could not conveniently be collected over water?
22. Mercuric oxide is stable up to 426° ; magnesium oxide to 2640° . Which of the two metals is the more active?
23. How may greatly lowering the cost of 90 to 100 per cent oxygen affect you personally?
24. Calculate the cost of oxygen (exclusive of heat costs) per 100 lbs. obtained from

Na_2O_2 at \$0.62 per lb.

KClO_3 " 0.51 " "

HgO " 1.46 " "

KNO_3 " 0.56 " "

Could you recover and sell any by-products?

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Chapter Outline

1. The Discovery of Oxygen.
2. Lavoisier's Great Mercury Experiment.
How did he prove that one-fifth of air is oxygen?
3. Occurrence of Oxygen.
4. Commercial Preparation.
5. Laboratory Preparation.
Do all substances rich in oxygen give it off on heating?
What compound gives off oxygen in contact with water?

6. Physical Properties of Oxygen.
Meaning of critical temperature and critical pressure of a gas?
7. Chemical Properties.
Six illustrations of combustion (equations).
Metals and non-metals.
Anhydrides.
Equations showing the reaction of some oxides with water.
Preliminary definitions of acids and bases.
What are oxides and how are they made?
8. Combustion.
Exothermic and endothermic reactions.
Meaning of heat of combustion of a substance.
9. Oxidation.
Common examples of oxidation.
10. Spontaneous Combustion.
11. Uses of Oxygen.
12. Influencing the Speed of Reaction.
Effect of temperature.
Effect of concentration.
Effect of catalysis.
Examples of catalysis.
13. Dust Explosions.
14. Ozone.
Occurrence in the air.
Properties.
Preparation.
Uses.
Test.
15. Allotropic Forms of Elements.

Review Suggestions

You have now studied five chapters. It is time to form the invaluable habit of *constantly reviewing*. Out of every two hours you use in preparation for a lecture spend one fourth of the time, half an hour, in review and make it the *first half-hour*. Otherwise you will find the time gone on the advanced lesson with no review. Your intention to catch up some day will be excellent, but such intentions are too often not made good.

Write equations constantly. Repeat those in the text and think up others to describe every reaction you have observed.

Do not read your lesson three times and assume that because you clearly understood every statement as you read it you have a thorough

grasp of the chapter. The test of your knowing the lesson is this. Can you shut the book and write an outline of the leading topics and then tell to yourself the leading facts under each topic head? Be as critical of your knowledge as your teacher may be on quiz day. Most students pamper themselves.

Skim the chapter to get a bird's-eye picture of it. Then carefully read the first topic once, shut the book, and tell yourself the main points of that topic. See if you are right. Read the next topic the same way. On finishing the last topic you will know the lesson.

Do not commit to memory the atomic weights. You will learn formulas by using them. Remember only the most important properties of substances.

Get a friend to open the text and quiz you on some chapter. Then quiz him on another chapter.

Chapter 7 GASES

It is a significant fact that any gas spreads (diffuses) through any other gas with great ease, almost as if the second gas were not occupying the given space. When we add the characteristic of nonsettling to such properties of gases as a great tendency to expand, great compressibility, great diffusibility, and great permeability, we are forced to explain how the structure of gases differs from the structure of liquids and solids. The gas laws immediately following lead into the kinetic theory of gases.

Boyle's Law. Boyle (1660) observed that *the volume occupied by a given sample of any gas varies inversely with the pressure, if the temperature is kept constant.* Accurate measurements showed that if the pressure was doubled on a given volume of a gas (keeping the temperature constant) the volume was reduced one-half. With three times the pressure the volume became one-third the original. This generalization can be formulated mathematically thus:

$$\frac{P_1}{P_2} = \frac{V_2}{V_1} \quad \text{or} \quad P_1V_1 = P_2V_2 \quad \text{or} \quad V_1 = V_2 \times \frac{P_2}{P_1}$$

where P_1 and V_1 are the first pressure and volume and P_2 and V_2 any other pressure with its accompanying volume. Since the product P_1V_1 is equal to any other pressure-volume product such as P_2V_2 for the same weight of the gas, it is sometimes said that the product of the pressure times the volume of a gas is a constant value. It is our custom to refer to the average atmospheric

pressure at sea level (enough to hold up a 760-mm. column of mercury in a barometer) as the *standard pressure*.

The simplest form of a barometer (on the right in Fig. 23) consists of a tube, over 760 mm. long, filled with mercury and inverted in a cup of mercury. The pressure of the air holds up the mercury in the tube to a height of about 760 mm. at sea level. If the tube is longer, there is a vacuum at the top. The cup may be dispensed with by using the form of tube represented on the left.

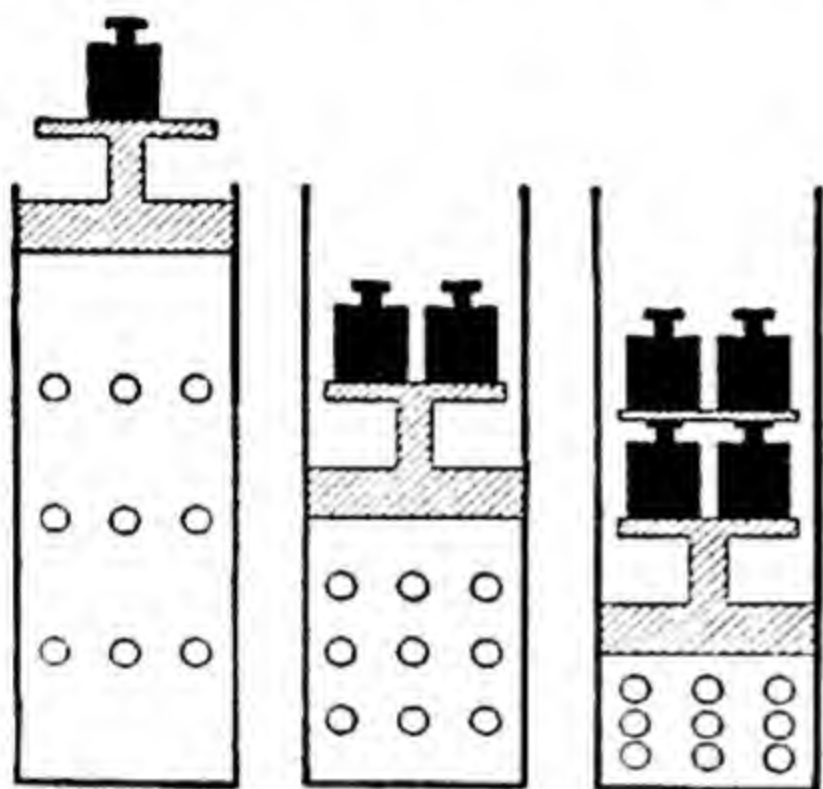


Fig. 22. The volume occupied by a given number of molecules of a gas varies inversely as the pressure.

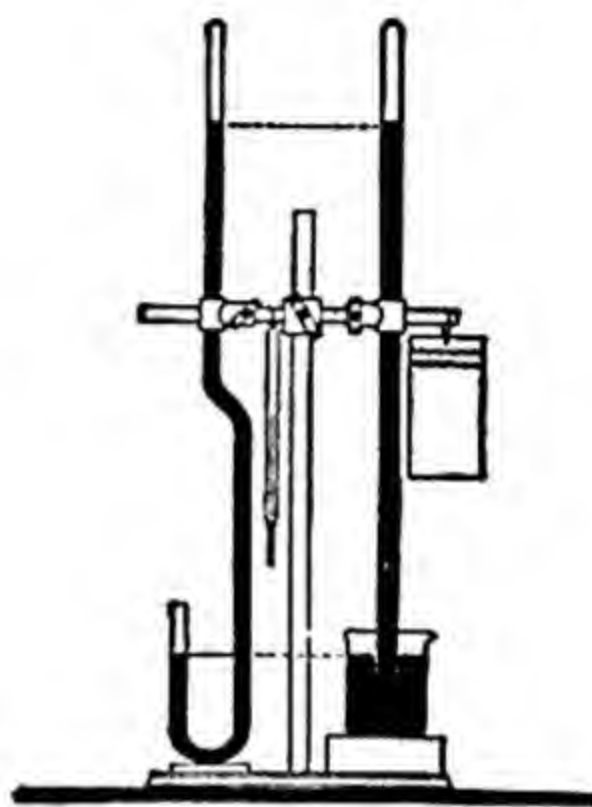


Fig. 23. Barometer (two forms).

Atmospheric pressure varies with the weather, the passage of high- and low-barometer areas sometimes causing a variation of 50 mm. or more in the barometric reading.

A man buying a million liters of a rare and expensive gas could be cheated if he failed to stipulate the pressure. Since gases expand indefinitely, a very small weight of a gas could occupy a million liters volume. We do not always measure gases at exactly 760 mm. pressure, but we calculate from Boyle's Law what the volume would be if the pressure were changed to the standard 760 mm. For example, 400 ml. of air at 740 mm. would occupy what volume at 760 mm.? Using the formula

$$V_1 = V_2 \times \frac{P_2}{P_1}$$

we may let V_1 represent the volume to be calculated and P_1 the standard pressure, 760 mm. To make it clearer

$$V_1 \text{ (standard)} = V_2 \text{ (observed)} \times \frac{P_2 \text{ (observed)}}{P_1 \text{ (standard)}}$$

Substituting, we have

$$V_1 \text{ (standard)} = 400 \times \frac{740}{760} = 389 \text{ ml.}$$

To aid the memory one merely recalls that the observed volume is multiplied by a fraction with the two pressures for its terms. Also if the change to 760 mm. means *greater* pressure, the gas will contract and therefore the numerator must be the smaller value. The calculation is similar if the change to 760 mm. means *less* pressure and consequent expansion.

The abbreviation "ml." stands for milliliter, approximately the same as the cubic centimeter, "cc."

Exercises

1. Convert 320 ml. of dry gas at 730 mm. to the volume at 760 mm.
2. Convert 560 ml. of dry gas at 775 mm. to the volume of 760 mm.

High Vacua. In spite of the great efficiency of devices for removing gas molecules from vessels, scientists never yet have obtained a vacuum in which one milliliter included fewer molecules than there are people on the earth.

The Langmuir vacuum pump, operating on the mercury vapor condensation principle, is used in connection with a backing pump capable of exhausting gases to a pressure only sufficient to hold up a column of mercury 0.1 mm. in height. With this as a start a lower pressure of 0.000002 mm. is readily obtained and *one-tenth* this is possible. "If from a liter vessel of gas there were removed 1,000,000 molecules a second, nearly 700,000,000 years would be required for the removal of practically all of the gas; but the Langmuir pump accomplishes this in two seconds." Even after exhaustion with a Langmuir pump a small electric light bulb would still contain twenty to thirty millions of millions

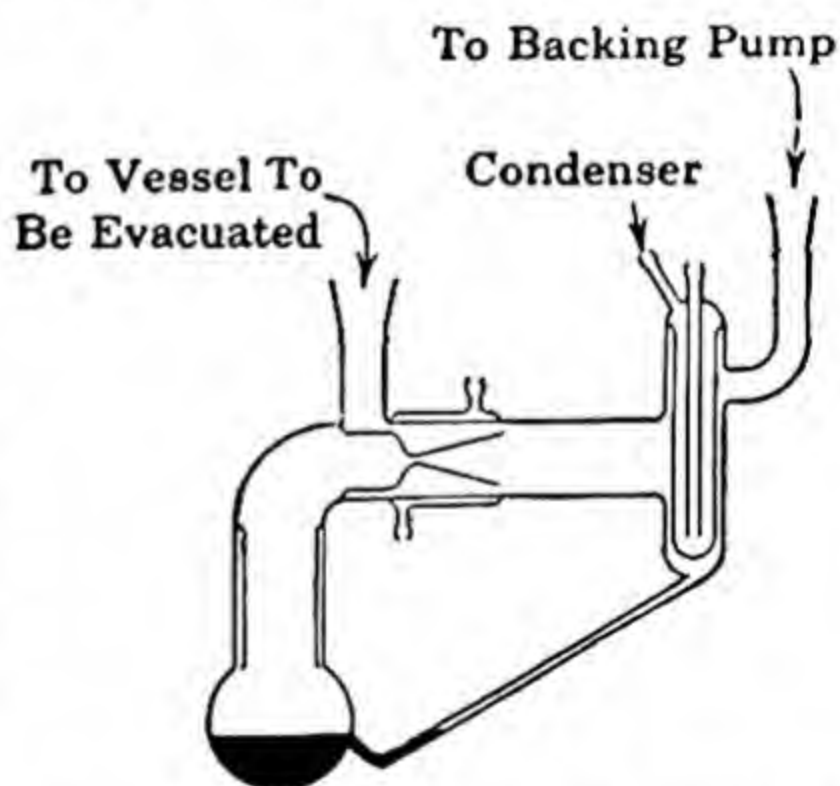


Fig. 24. A vacuum pump that uses a stream of vapor from boiling mercury (condensed and returned) to sweep out gases.

of molecules. To find a nearly perfect vacuum we should have to go out to interstellar space where, in the volume of a common electric light bulb, there seem to be only one or two hundred gaseous molecules. High vacua, or even partial vacua, minister to our comfort and serve well in many ways. They made possible the original incandescent lamp (although the type has since changed), the X-ray tube, the radio tube, the photoelectric cell of television, the thermos bottle, and increased the efficiency of steam engines and turbines. High-vacuum distillation has been adopted by industry.

At the opposite extreme are the high gas pressures developed by explosion in the largest cannon, up to 45,000 p.s.i., pounds per square inch.

Charles' Law and the Absolute Temperature. Charles in 1787 observed that on cooling any gas from 0°C. to -1°C. it

contracted $\frac{1}{273}$ of its volume. It was a simple inference that if cooled 273°C. below 0°C. its volume would be nothing at all. However, in practice all gases become liquid before they have been cooled 273°C. below 0°C. , and after it becomes liquid a substance no longer obeys the gas laws. There is a real convenience, however, in calling this imaginary point of no translational or random motion of molecules **absolute zero**, -273°C. , very accurately, -273.16° .

In honor of the eminent physicist, Lord Kelvin, this temperature is usually termed 0°K.

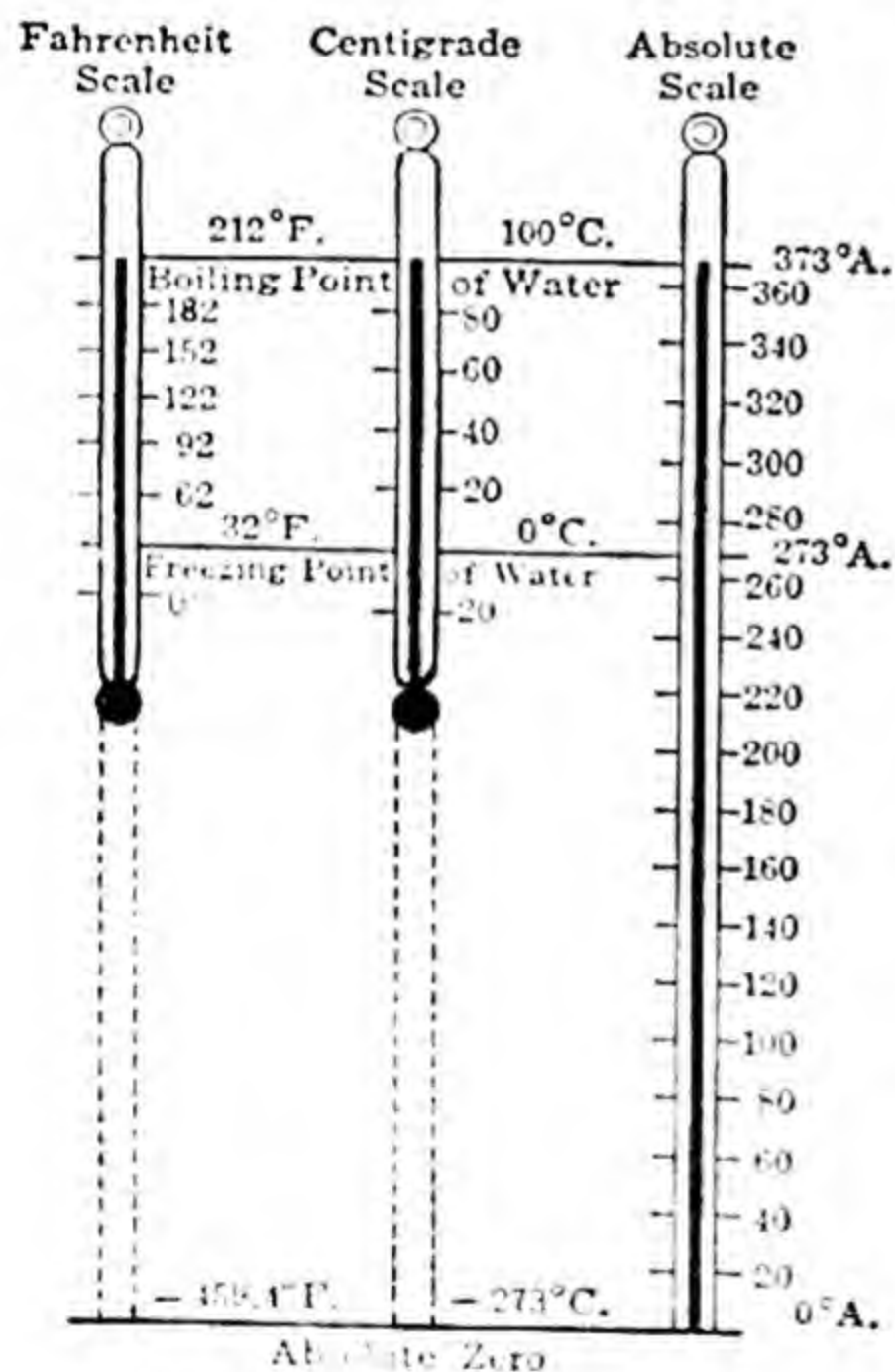


Fig. 25. Thermometer scales.

At absolute zero the atoms or molecules of solids have little if any kinetic energy, but the electrons probably have motions and energies of a high order. The most difficult gas to liquefy is helium, which must be cooled to -268.7°C.

Temperature is a measure of the condition that determines direction of transfer of heat from one body to another.

Figure 25 shows the relations between the two temperature scales. To change from a Centigrade reading we merely add 273° to get the absolute temperature. For example, $17^{\circ}\text{C.} = 17^{\circ} + 273^{\circ} = 290^{\circ}\text{K.}$

3. Convert -56°C. into the absolute temperature.

Charles' Law is merely an observation that *the volume of a given sample of a gas varies directly as the absolute temperature* (if the pressure is kept constant). For example, to double the volume that a gas occupies at 20°C. we should need to heat it not to 40°C. but to twice the absolute temperature. The temperature $20^{\circ} + 273^{\circ} = 293^{\circ}\text{K.}$ Twice this is 586°K. or 313°C.

When heated to 586°K. , the gas would have twice its original volume. Charles' Law is, therefore, formulated as follows:

$$\frac{V_1}{V_2} = \frac{T_1}{T_2} \quad \text{or} \quad V_1 = V_2 \times \frac{T_1}{T_2}$$

where T_1 and T_2 refer to absolute temperatures. When we speak of a liter of oxygen weighing 1.429 g., we mean a liter at 760 mm. pressure and 0°C. Since gases expand on heating, there can be no accuracy without reference to a definite *standard temperature*. Obviously we do not care to measure gases in rooms at 0°C. , but we can apply Charles' Law and calculate what the volume *would be* if the gas were cooled to 0°C. For example, what is the volume of 400 ml. of air measured at -18°C. when warmed to 0°C. ?

$$V(\text{standard}) = V(\text{observed}) \times \frac{273}{273 \pm t^{\circ}}$$

where t° is the Centigrade temperature. Substituting values

$$V(\text{standard}) = 400 \times \frac{273}{255} = 428 \text{ ml.}$$

One should note that the observed volume is multiplied by a fraction with absolute temperatures for its terms and that if the change is to a *higher* temperature the gas will expand, occupying more volume; therefore the numerator must be larger than the denominator. The observed volume of a gas can be brought to 760 mm. and 0°C. by applying both corrections at once. For

example, 400 ml. of air at 740 mm. and -18°C . would have what volume at standard temperature and pressure?

$$V(\text{standard}) = V(\text{observed}) \times \frac{760}{740} \times \frac{273}{255} = 417 \text{ ml.}$$

It also follows from Charles' Law that for each degree rise in temperature the pressure of a gas increases by $\frac{1}{273}$ if the volume is kept constant.

When gasoline explodes (with fifteen times its own volume of air) in an ordinary auto engine, approximately 58 volumes of all

the gases concerned are converted into new substances that would occupy about 62 volumes if kept at the same temperature as before. The great increase in pressure actually observed must be due to the very high temperature of reaction which makes the molecules (almost the same number as before) move with greater velocity. Yet 40 per cent of the heat is lost with the exhaust.

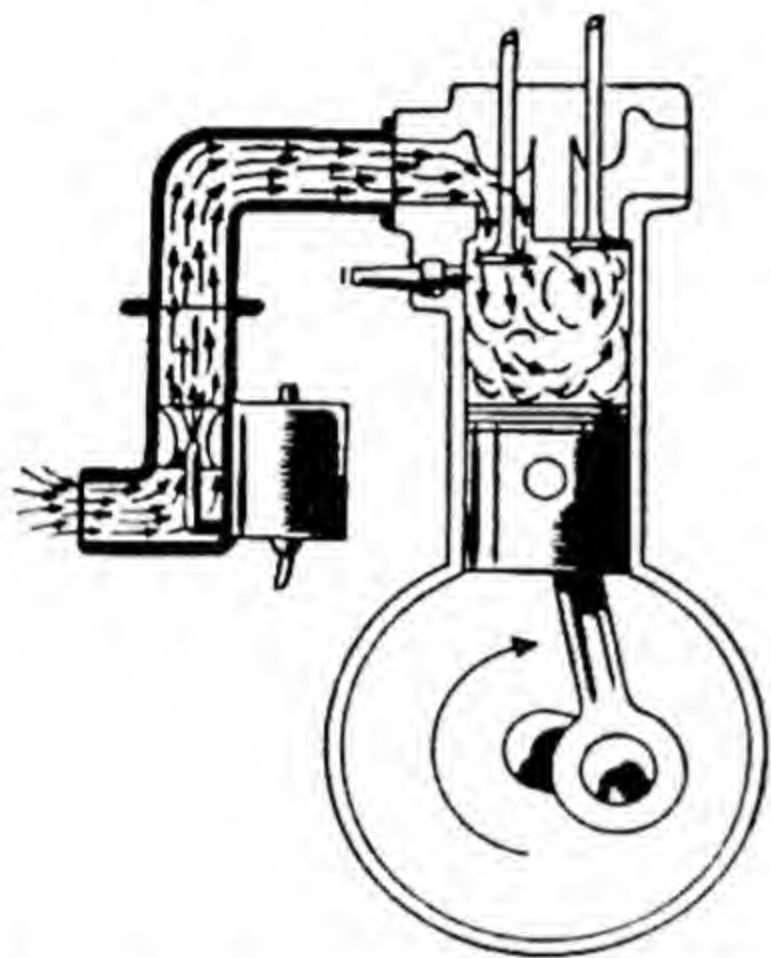


Fig. 26. Charles' Law is mainly responsible for movement of the piston in an automobile cylinder.

The effect of Charles' Law is evident in jet propulsion airplanes and rockets. Air, compressed by power from the gas turbine, meets fuel and spark to burn in an alloy

steel tube. At the high temperature resulting the greatly increased volume of all the gases entering or formed exerts pressure against a jet turbine operating the compressor and, in escaping through an opening, exerts a powerful backward thrust. It is this thrust that moves the plane at 600 miles per hour, or faster.

In the Diesel engine the work done in compressing the air alone (first step in operation) raises the gas temperature to 538°C . When fuel oil is sprayed into this hot mixture it ignites explosively.

4. Convert 890 ml. of gas at 14° and 775 mm. to its volume at 0° and 760 mm.

The pressure required to prevent expansion of a gas on heating varies directly as the absolute temperature. When TNT explodes the volume of the hot gases formed is 2360 times that of the TNT.

NOTE: Distinguish carefully between temperature and quantity of heat. One degree change in temperature does not correspond to one calorie except when it concerns one gram of water.

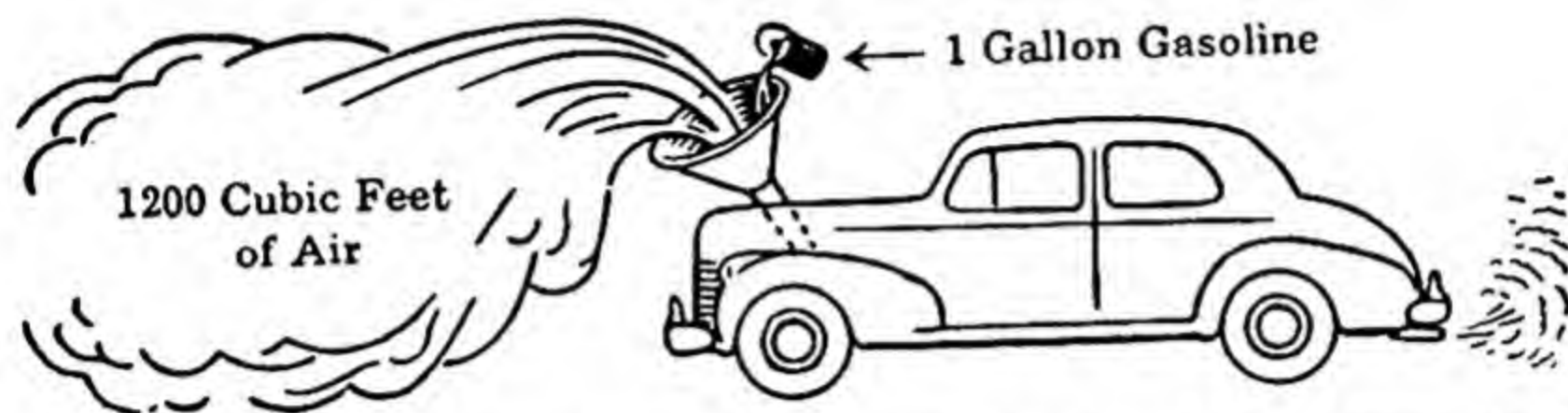


Fig. 27. The chemical energy locked up in gasoline is released by reaction with the oxygen of the air. Heat of reaction expands the gases formed. (Courtesy General Motors Corporation.)

It is hard to believe but there is more power in gasoline than in an equal weight of nitroglycerine.

In 1597 the first thermometer was invented (by Galileo); in 1721 the Fahrenheit scale; in 1742 the Centigrade scale; and in 1880 the present clinical thermometer, invaluable aid to the physician.

Low Temperatures. Onnes induced an electric current in a lead ring at 1.7° K. The electric resistance was so low that current continued to flow for some time after the exciting cause was gone.

Although Onnes cooled helium, by evaporation of its own liquid form, to within one degree of absolute zero, he believed that it would remain fluid even at 0° K. However, in July, 1926, only a few months after the death of Onnes, his associate Keesom, at the University of Leyden, froze helium to a solid at 0.9° K. under 28 atmospheres pressure. In 1935 DeHaas at Leyden announced a new low temperature, only 0.0044° above Absolute Zero. Liquid air was used to cool compressed hydrogen until it liquefied; the liquid hydrogen upon evaporation produced a further cooling effect sufficient to liquefy chilled and compressed helium, which upon expansion produced further cooling.

The final stage depended upon the heat effects in magnetization of certain paramagnetic salts. More recently 0.003° K. has been reached. A salt of great magnetic sensitivity such as $\text{Gd}_2(\text{SO}_4)_3 \cdot 8 \text{H}_2\text{O}$ or $\text{K} \cdot \text{Cr}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$ is sealed in a small container with helium gas. This tube is surrounded by liquefied helium in a Dewar flask. The apparatus is then placed in a magnetic field where

some of the magnetic energy is changed to heat by the sensitive salt. The warmed-up helium gas is pumped off and the magnetic field broken. The reverse effect, lowering of temperature, is then observed.

At such extraordinarily low temperatures some metals and alloys show almost no resistance to the passage of the electric current. Following the example of Onnes, a startling demonstration of this property was used by McLennan to entertain the Royal Institution in London. "I exhibited to the audience a closed ring of lead immersed in liquid helium and carrying a current of more than 200 amperes. The current had been started (by induction) in the superconducting lead ring some six hours earlier in the afternoon by Prof. Keesom in Leyden, and it persisted undiminished in intensity while being transported by aeroplane to London." Pure lead suddenly becomes superconducting at 7.2° Abs. (or K.) while mercury must be cooled to 4.22° K. Gold remains indifferent.

At temperatures approaching Absolute Zero, quartz conducts electricity as well as copper does at room temperature.

Low temperature (-50° C.) is utilized by the oil refinery in removing paraffin wax.

Systems of thermometry depend for their accuracy upon sharp changes of state such as the freezing of water, boiling of water, and melting points of various elements or pure compounds. Con-

sequently the accurate determination of 3810° K. as the vaporizing temperature of carbon in the arc gave us a much needed reckoning point in the upper temperature range.

Law of Partial Pressures. Dalton noted that the total pressure of a mixture of gases was the sum of the pressures that would be exerted by each gas if the others were not present (temperature being the same). All gases collected or measured over water have water vapor present, which exerts a part of the total pressure. To learn the actual pressure exerted by the dry gas we must subtract the pres-

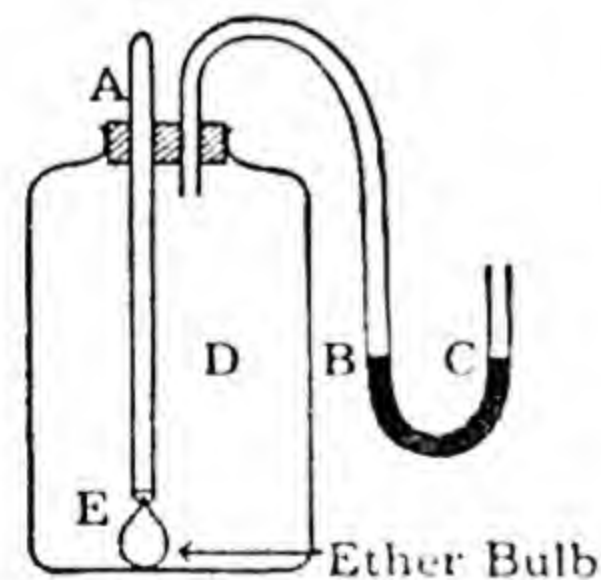


Fig. 28. When the bulb of thin glass at E is broken by pressing down A, ether vaporizes and adds its partial pressure to that of air in D. Liquid falls at B and rises at C.

sure due to water vapor at the given temperature. To show how the values for the pressure of water vapor can be obtained we can fill a tube over 760 mm. long with mercury and, closing

the end with a thumb, invert the tube, placing the open end in a dish of mercury. The mercury is held up to some definite height, depending on the pressure of the air, 760 mm. at sea level. We have thus a simple form of the *barometer* for measuring air pressures. If, now, we force a few drops of water (by a medicine dropper) under the tube, the water rises into the vacuum at the top, a part of it vaporizes, and the vapor exerts pressure downward on the column of mercury. The mercury falls a certain distance, which depends upon the temperature. To determine the vapor pressures at different temperatures the tube can be surrounded with a jacket through which flows water at desired temperatures. A table of "aqueous tension" values is given in the Appendix. Since we measure most gases over water, the gases are saturated with moisture at the given temperatures.

Suppose the problem is to correct to standard conditions 400 ml. of air collected over water at 740 mm. and 18° C. Now the *observed pressure* of 740 mm. is not all due to the air, for 15.5 mm. of it is due to water vapor. Therefore, subtracting the aqueous tension from the barometric reading,

$$V_1 \text{ (standard)} = V_2 \text{ (observed)} \times \frac{740 - 15.5}{760} \times \frac{273}{291} = (?) \text{ ml.}$$

NOTE: A table of corrections for the expansion of the mercury column due to heating above 0° C. is found attached to some barometers.

5. Convert 424 ml. of air measured over water at 21° C. and 785 mm. to the volume under standard conditions.

Graham's Law of Diffusion. All gases mix homogeneously unless they react. Bromine is a heavy gas, but if a little is released at the bottom of a tall cylinder of air, the bromine can soon be smelled at the top, rising against the force of gravitation.

Graham measured the rates at which gases diffuse through minute holes and found that *the speed of diffusion of gases varies inversely as the square roots of their densities*. Oxygen is about sixteen times as heavy as hydrogen, hence hydrogen diffuses four times as fast as oxygen. Let R_1 represent the rate of diffusion for

oxygen and R_2 the rate for hydrogen; D_1 the density of oxygen and D_2 the density of hydrogen:

$$\frac{R_1}{R_2} = \frac{\sqrt{D_2}}{\sqrt{D_1}} = \frac{\sqrt{1}}{\sqrt{16}} = \frac{1}{4}$$

6. A liter of carbon dioxide (at 0°C . and 760 mm.) weighs 1.9768 g. and a liter of nitrogen weighs 1.2507 g. Compare their rates of diffusion accurately.

Professor W. H. Chapin at Oberlin once was asked to determine the amount of recoverable gasoline in a certain sample of natural gas. Remembering Graham's Law he allowed equal

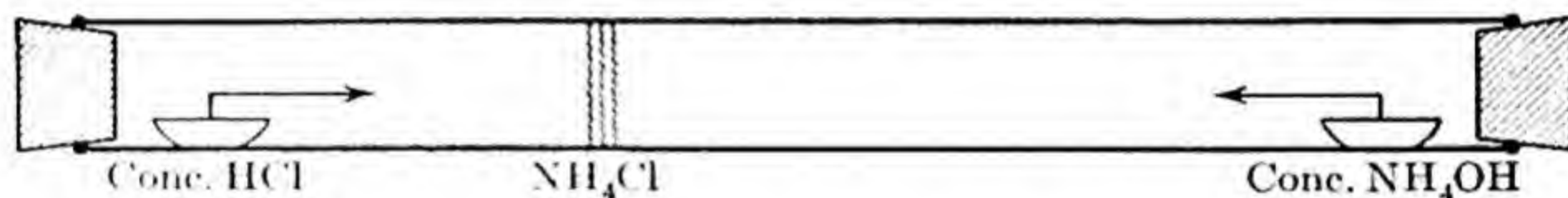


Fig. 29. Graham's Law is illustrated by Chapin's experiment. Within the long glass tube lighter NH_3 molecules diffuse faster than heavier HCl molecules, as shown by the position of a ring of white NH_4Cl formed where they meet.

volumes of this gas and of dry air to diffuse (separately) under the same pressure through a porous clay cup (full of small holes). Knowing the average molecular weight of air he calculated from the time of diffusion the average molecular weight of natural gas. From tables at hand the percentage of gasoline present was easily known.

Graham's Law was applied during the last war in an effort (successful) to isolate the explosive kind of uranium for use in the atomic bomb. A volatile fluoride of uranium diffused through a barrier wall containing minute holes, at a rate somewhat different from that of other volatile impurities present. Industry may apply this technique to separation of helium from natural gas and to other gas separations.

The Kinetic Theory of Gases. To explain the facts expressed in the laws of Boyle, Charles, and Dalton, as well as certain other facts, it is believed that the molecules of a gas are relatively very far apart; that they move rapidly in straight lines until they collide with other molecules, yet rebound with such perfect elasticity

that there is no loss of motion; and that gas pressure is caused by the impacts of gas molecules. The theory that gas pressure is produced by the impacts of separate moving particles is in accord with the facts of gas pressure. The walls of containing vessels are pounded with a hailstorm of particles moving, at 20°C. , at a speed of about one mile per second in the case of hydrogen.

Reliable experimental evidence has recently shown that at 0°C. and 760 mm. 1 ml. of any gas contains 2.7×10^{19} molecules and yet the average distance between molecules is about ten times their average diameter.

Cohesion between molecules of a gas counts for very little because they are so far apart and, at elevated temperatures, moving with such great velocity. But on cooling, their kinetic energy decreases and the molecules may come close enough to each other to allow their mutual attraction (cohesion) to become a powerful factor. The gas may then become a liquid. At very high pressures, then, gases decrease in volume more than could be predicted by Boyle's Law, due to this helping effect of cohesion. There is another factor which introduces a deviation from the gas laws. At ordinary pressures a liter of gas is mainly space, but when highly compressed the part of the total volume occupied by actual molecules becomes noticeable. Since Boyle's Law holds only for the change in free space, it loses in accuracy at high pressures.

In any gas some molecules have greater kinetic energy than others. We are most concerned with the average.

As was stated before, a very small mass of any gas expands indefinitely, filling any vessel no matter how large. Pressure is exerted on all walls of such a vessel. This could not be true if gases exerted pressure like the thrust of a spring or the downward and sidewise thrust of a liquid. Gas pressure is exerted in all directions and has no limit in distance. The spring has its limit.

In liquids and solids cohesion is a tremendous factor because the molecules are in frequent contact. Yet the molecules are moving even here, although in shorter free paths. Evaporation of liquids, their vapor tension, and the fact that increase of temperature transforms solids and liquids into gases, all confirm this

view. Mercury is easily volatilized, but we are thankful that tungsten is not, for otherwise tungsten electric lamps would not last long.

Absolute Zero now takes on a new meaning. It is the temperature of no translational molecular motion although the nucleus may spin and electrons revolve.

Van der Waals' Equation is a correction of Boyle's Law based upon allowances for the forces of cohesion and the actual space occupied by the molecules.

Critical Properties. When compressed the molecules of a gas can be brought so close together that their own attractive forces restrict their motion greatly and liquefaction results. The lower the temperature the less the pressure required to overcome the kinetic energy of the molecules. Yet for every gas there is a temperature above which no pressure, however great, can overcome this kinetic energy and produce liquefaction. This is called the **critical temperature** (155°K. for oxygen). The pressure required to liquefy a gas at its critical temperature is its **critical pressure** (49.5 atmospheres for oxygen).

Liquefaction of gases by pressure is comparatively easy for ammonia, chlorine, carbon dioxide, and sulfur dioxide, but both high pressure and great cooling are required to liquefy such gases as oxygen, nitrogen, hydrogen, and helium. In fact it is not so long ago that scientists referred to

the "five permanent gases." Now they have all been liquefied, thanks to the aid of better methods of securing very low temperatures. Of course it is hopeless to attempt the liquefaction of oxygen until this gas is cooled below " 155°K. " Sometimes the gases that can be liquefied by pressure alone at room temperature are called "vapors."

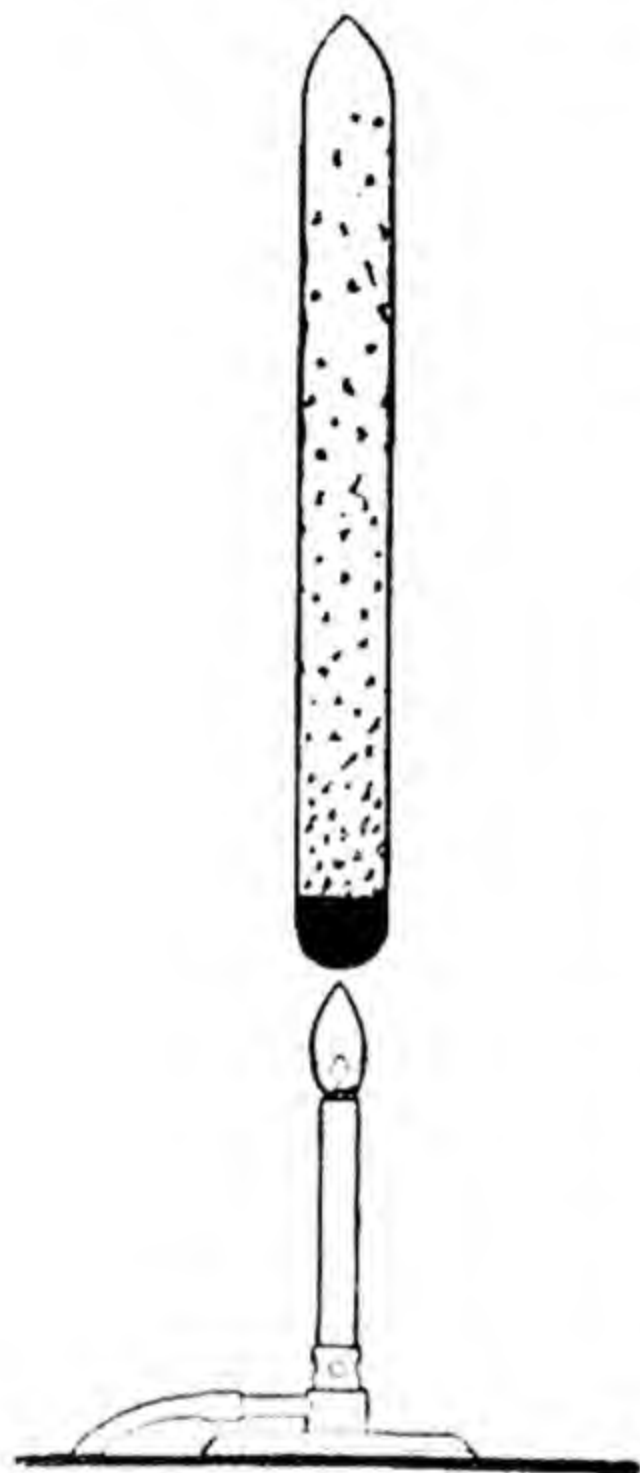


Fig. 30. In this glass tube mercury and bits of blue glass are sealed in a moderate vacuum. When the mercury is cautiously heated, without boiling, the increased molecular bombardment by heavy mercury molecules knocks the bits of blue glass to the full height of the tube, possibly 25 cm.

Avogadro's Law. Some of the preceding facts led Avogadro in 1811 to the theory that *equal volumes of all gases at the same temperature and pressure contain equal numbers of molecules*. Until 1860 science paid little attention to this speculation, but we are now convinced of its truth.

Gases must be composed of flying molecules because such a kinetic theory explains the observed facts:

FACTS	EXPLANATION
1. Ease of diffusion	Relatively wide spaces between flying molecules
2. Great compressibility	A given volume of gas is mostly space
3. Gas pressure extends in all directions	The molecules fly in all directions and bombard the walls of the containing vessel
4. Boyle's Law	Pressure crowds molecules closer together
5. Charles' Law	Molecules fly faster with rise in temperature
6. Boyle's Law and Charles' Law both fail when gases are nearly liquefied	The gas laws refer to change in the amount of free space between molecules rather than to total volume; at high pressures the molecules themselves occupy a very appreciable fraction of the total volume; also cohesion between molecules aids compression
7. Liquefaction of gases	Forcing molecules into rather close contact brings in the aid of molecular attraction in restricting freedom of movement
8. Evaporation of liquids	Molecules at the surface of liquids escape beyond the range of attraction of the liquid
9. Each gas in a mixture exerts the same pressure it would show in absence of other gases	Molecules have plenty of room for free movement; since they are perfectly elastic, collisions between them cause no loss of motion, merely change the direction of motion

Exercises

(Unless otherwise stated gas volumes are measured at 0° and 760 mm.)

7. Convert 25° C. to the Fahrenheit reading; 90° F. to the Centigrade reading.
8. A given quantity of gas has a volume of 15 liters at 780 mm. On coördinate paper plot a curve showing the application of Boyle's Law when the pressure is changed to 150 mm., 200 mm., 250 mm., 300 mm., and 500 mm.
9. A liter of oxygen at 760 mm. is forced into a vessel containing a liter of nitrogen at 760 mm. What will be the resulting pressure?
10. Could you use water instead of mercury in a barometer?
11. In the tropics drinking water is cooled by storing it in porous jars. Explain.
12. How well would a tungsten lamp work at 1.7° K.?
13. If a liter of gas were heated in a strong container, what would happen as the temperature rose 1° C.? The gas could not expand by $\frac{1}{273}$ in accordance with Charles' Law, yet the rise in temperature is accompanied by greater kinetic energy of the molecules.
14. Why is so much energy required to change water at 100° C. into steam at 100° C.?
15. The density of gases is referred to oxygen, hydrogen, or air. If air is taken as a standard (density of 1), what is the relative density of carbon dioxide? One liter of air weighs 1.293 g. and one liter of carbon dioxide weighs 1.976 g.
16. A gas collected over water at 18° C. has a volume of 500 ml. when the pressure is 755 mm. What would be the volume of the dry gas at 0° C., 760 mm.? (The partial pressure of water vapor over water at 18° C. is 15.4 mm.)
17. The volume of a given sample of gas at 740 mm. and 9° C. is 480 ml. What will be its pressure when its volume is 20 ml. and its temperature 15° C.?
18. A gas occupies a volume of 200 ml. when measured over water at 22° C. and 730 mm. What volume will it occupy, dry, at standard conditions?
19. Define critical temperature, absolute zero, associated molecules, fractional distillation, surface tension, viscosity, freezing point, heat of fusion. Next chapter.
20. On coördinate paper plot the Centigrade scale from -40° C. to 100° C. on one axis and the Fahrenheit scale from -40° F. (curiously enough, identical with -40° C.) to 212° F. on the other axis. Complete the square and draw a heavy line from the origin (-40° C.) diagonally to the opposite corner. By reading intersections on this "curve" convert any temperature on one scale into its equivalent on the other.
21. How many grams of water could be heated from 0° C. to 80° C. by the heat required to melt 12 kilograms of ice at 0° C.? Next chapter.

22. Avogadro's No., 6.03×10^{23} , is the number of molecules in a mole (G. M. Wt.). Calculate the number of molecules of a gas under standard conditions of temperature and pressure in 180 ml. One mole of any gas under standard conditions occupies 22.4 liters.
23. Convert 850 ml. of a dry gas at 28°C . and 720 mm. to its volume at -10°C . and 700 mm.
24. If the average distance between molecules of a gas (standard conditions) is ten times the diameter of a molecule what fraction of the total volume is due to actual molecules?
25. The volume of a given sample of gas at 750 mm. and 22°C . is 690 ml. The pressure is reduced to 600 mm. At what temperature would the gas occupy its original volume under this new pressure?
26. The density of a gas relative to air is 5.2. What is the volume occupied by 10 g. at 20° and 752 mm.?
27. Carbon dioxide (22 times relative density of hydrogen) diffuses 0.212 times as fast. Is this in accord with Graham's Law?

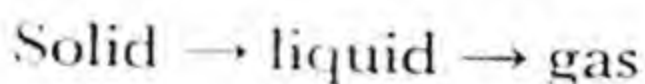
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Chapter 8 LIQUIDS AND SOLIDS

The Three States of Matter. Solids retain their shape, liquids take the shape of the containing vessel, but gases expand indefinitely. There is great freedom of molecular movement in gases and comparatively little in solids and liquids. Whether a substance is in the solid, liquid, or gaseous state at a given temperature and pressure depends on the relative influence of the forces of cohesion and the kinetic energy of the molecules.

Transformations. Kinetic energy must be added to the molecules in order to bring about the change:



The forces of cohesion must be overcome in order to allow the increased freedom of molecular motion called for by the change of state.

LIQUIDS

In liquids there is no orderly arrangement of molecules (with the exception of the rather unusual liquid-crystals). Yet in such liquids as water, alcohol, and acetic acid some of the molecules are "*associated*" in groups, the proportion of such associated molecules varying with the temperature. Steam, for example, is made up of single molecules, while liquid water contains $(\text{H}_2\text{O})_3$ as well as $(\text{H}_2\text{O})_2$ and simple H_2O . The freedom of movement of molecules in liquids is such that at the surface molecules with

sufficient kinetic energy fly off into the space above, or, in other words, *evaporate*. Some of these fugitive molecules, now in the vapor state, return to the liquid (because of the irregular molecular paths) and are held, at least temporarily, by the forces of cohesion. The rate of evaporation increases with rise in temperature, and the vapor tension of the liquid shows a steady increase until the upward thrust of escaping molecules just equals the downward thrust of all gaseous molecules immediately above the liquid surface. At this temperature the liquid *boils* with violent breaking of the surface.

Only molecules with greater than the average kinetic energy break through the surface film of liquid molecules.

Boiling Point. *The boiling point of a liquid is the temperature at which its vapor tension equals the pressure of the atmosphere above it.* Obviously the boiling point varies with the pressure of

the atmosphere. Water boils at 100°C . under an atmospheric pressure of 760 mm., but at one-half an atmosphere it boils at 82°C . and at 4.6 mm. pressure it boils at 0°C . At two atmospheres the boiling point is 121°C . Boiling points recorded in the text all refer to the standard atmospheric pressure, 760 mm. The ebullition observed in any boiling liquid is due to the expansion of bubbles of vapor forming within the liquid. Water has a relatively high *heat of vaporization*, requiring 539 cal. to change one gram of water at 100°C . into steam at 100°C . The heat of vaporization of ether is only 84 cal. per g. Obviously when one gram of steam at 100°C . condenses to liquid water at 100°C ., the same amount of heat, 539 calories, is given off as *heat of condensation*.

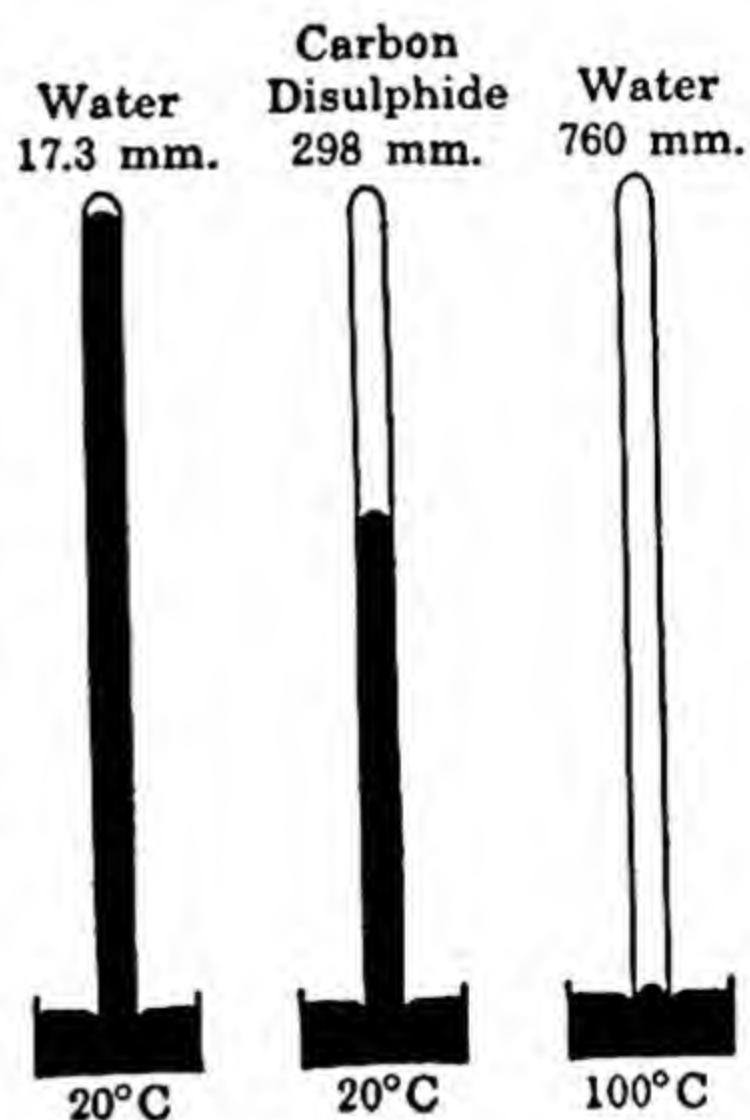


Fig. 31. Vapor pressures at different temperatures.

The vapor pressure of a liquid becomes "vapor tension" when vapor and liquid are in equilibrium.

The boiling point of any pure liquid at 760 mm. pressure remains constant (100°C . for water, 78.3°C . for alcohol, etc.) until all the liquid has changed into vapor. Not so with mixtures of two or more liquids. For example, alcohol-water may start boiling somewhat above 78.3°C ., but the temperature steadily rises, with escape of vapor of steadily varying composition. After repeated distillation, as in the column still, the distillate attains a concentration of 95 per cent alcohol, the common commercial product.

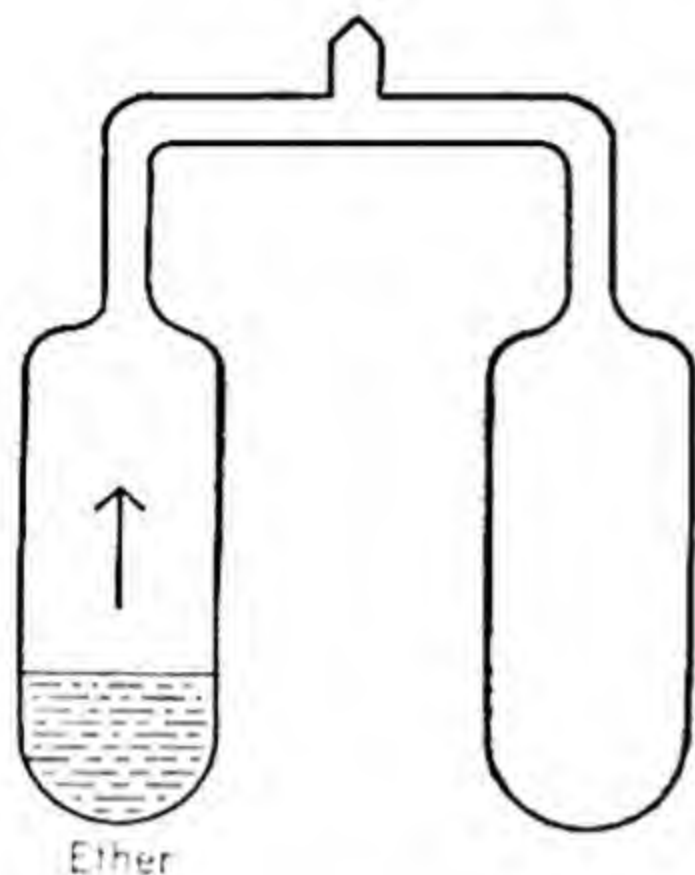


Fig. 32. When the empty bulb on the right is surrounded with a beaker of "dry ice" the ether in the bulb on the left boils, soon condensing to liquid on the right. Later the process may be reversed by chilling the bulb on the left after removing the dry ice from the right. Most of the air has been pumped out by the glass blower before sealing the tube at top. (Courtesy Dr. Fred Dutton.)

Similarly a pure solid melts sharply at a definite temperature, characteristic of that substance, unless decomposed by the heating. Mixtures of two or more solids melt through a range of temperatures.

Water in the teakettle absorbs heat from the flame while boiling. Liquefied sulfur dioxide in a beaker resting on the table, not on the stove, will boil, absorbing heat from its surroundings, as it does in the coils of your refrigerator. The boiling point of liquefied sulfur dioxide is -10°C . and that of liquefied ammonia is -33.5°C .

Distillation. The process of evaporating and recondensing a liquid (by cooling) is termed *distillation*. To expedite matters the liquid is usually boiled, sometimes under less than atmospheric pressure. This *vacuum distillation* is desirable with liquids or solutions likely to decompose at the normal boiling temperature. Of course with diminished pressure of vapors above a liquid, less kinetic energy and a lower temperature are required for boiling. In Fig. 33 is shown ordinary laboratory distillation.

Surface Tension. The surface film of a liquid is in an apparent state of tension due to the unbalanced attractions between mole-

cules at the surface as compared with those in the body of the liquid which are entirely surrounded by other molecules. Liquids with high inter-molecular attraction (difficult to boil) tend strongly to take the spherical form, with least surface, and consequently have high surface tension: mercury is a notable example. Water and ether are examples of liquids with much lower surface tension. Soap lowers the surface tension of water so that it can creep in between particles of dirt, thus dislodging them.

Viscosity. The term *viscosity* is used to denote the resistance due to internal friction which substances offer to deforming forces. (A viscous substance is

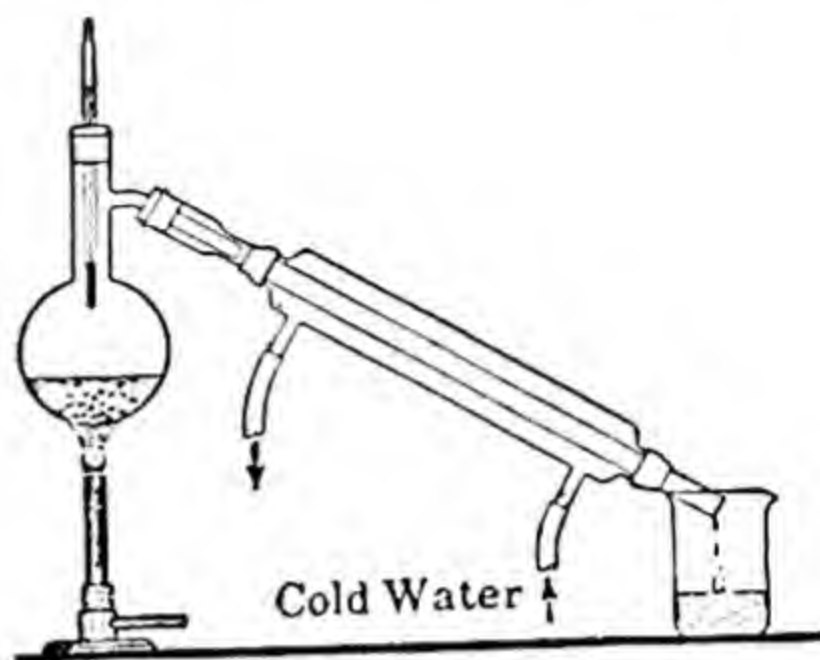


Fig. 33. Purifying water by distillation.

deformed permanently to a degree directly proportional to the deforming force.) Molasses and glycerine are typically viscous liquids, although their viscosity decreases with rise in temperature — they become more “fluid.”

SOLIDS

Freezing Point of Liquids. When liquids are cooled sufficiently they lose their fluidity and take on rigidity. They freeze to solids without further lowering of temperature until all the liquid has solidified. When the change of state occurs at a definite temperature the solid formed is always crystalline.

Glasses and tars, however, do not change state suddenly at a sharply definite temperature. In fact they act like undercooled liquids. Glycerine, suddenly chilled in liquid air, solidifies before it has time to crystallize, becomes glass-like. Even water may be chilled below 0°C . without separation of ice crystals. However, the addition of a minute fragment of ice starts crystallization or freezing. Consequently we are forced to *define the freezing point (same as melting point) as the temperature at which liquid and solid will remain in contact with each other without change of temperature.*

At this temperature the vapor tension of solid and liquid must be equal or one form would be converted into the other by evaporation and condensation.

Solids, maintaining shape and volume, are crystalline according to the strictest interpretation. Glass and pitch are "apparently solid," yet under sufficient stress they show flow if stress is applied slowly.

There is little attraction between the molecules of such substances as CH_4 , C_2H_6 , etc., hence they exhibit no association in the liquid state and have low boiling points; and low freezing points.

Melting Point and Heat of Fusion. To increase the freedom of movement of the molecules of a solid so that a fluid results requires energy. This is supplied by heating the solid. Heat breaks up the crystalline arrangement of a solid. There is a rise in temperature until some liquid is formed and then no further rise until all the solid is melted. Any additional kinetic energy given the liquid first formed is used in tearing off molecules of the solid. To convert one gram of ice at 0°C. into liquid water, 79.7 cal. of heat are required. This is termed the *heat of fusion* of ice. The corresponding value for sulfur is 9.37 cal. and for aluminum 76.8 cal.

Amorphous solids, unlike crystalline solids, have no definite melting points, and no definite heat of fusion.

The boiling point of water (100°C. at 760 mm. pressure) is used in standardizing thermometers. Another and more accurate fixed point is the melting point of pure benzoic acid (122.37°C.). This is accurate to one thousandth of one degree.

Melting point pellets, melting in steps of 25°C. and useful in checking furnace temperatures, are sold by the Central Scientific Co., Chicago, and by other dealers.

Vapor Pressure of Solids. At the surface of solids there is less freedom of movement than at liquid surfaces and yet molecules evaporate from many solids. Wet clothes dry at temperatures below 0°C. , and a crystal of iodine left in the open evaporates and shows a very noticeable vapor pressure. Camphor, like iodine, volatilizes rapidly just below its melting point. Solids that

pass directly into the vapor state without melting are said to *sublime*.

Crystal Systems. When a liquid solidifies, it usually is found to be made up of particles of regular geometric form called crystals. Crystals are formed also by evaporation of solutions or cooling of some vapors. Crystals often mass together so as to make their individual forms indistinct, that is, we have a crystalline mass. Perfect crystals have plane surfaces meeting at definite angles and their edges are straight lines. These plane surfaces are arranged with reference to imaginary lines, called axes of symmetry, drawn through the crystal. By the relative lengths and angles of intersection of these axes we can define the *six crystal systems*.

“An axis of symmetry is a line about which the crystal may be rotated so that it presents exactly the same appearance more than once in a complete revolution.” Three (sometimes four) axes of symmetry (lines meeting at a point) determine crystalline form in the six systems.

1. Isometric or cubic system: three axes of equal length at right angles to each other. Examples: alum, sodium chloride, potassium iodide, iron pyrites, and lead.

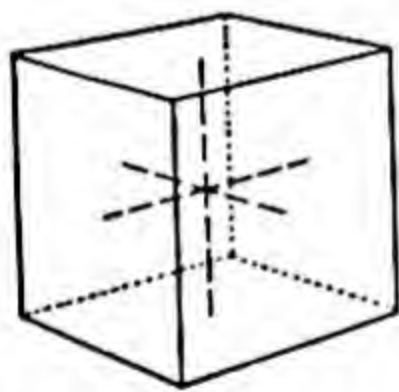


Fig. 34. Cubic.

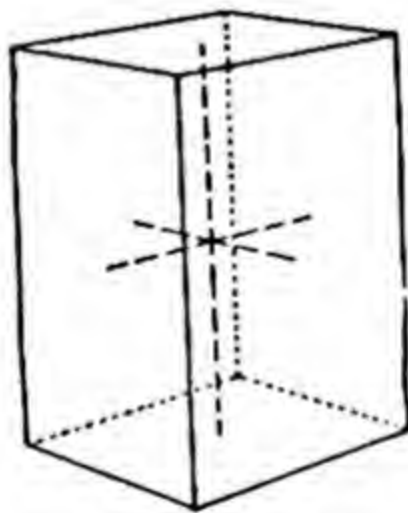


Fig. 35. Tetragonal.

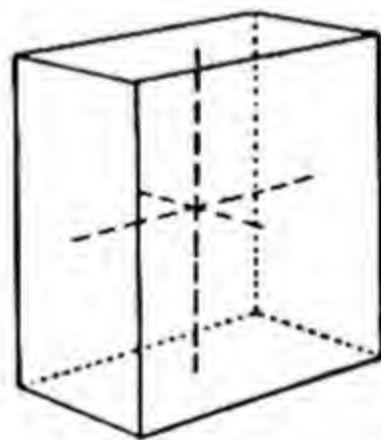


Fig. 36. Rhombic.

2. Tetragonal system: two equal axes and one of different length, all at right angles to each other. Examples: nickel sulfate and urea.

3. Rhombic system: three unequal axes, all at right angles (Fig. 36). Examples: sulfur, zinc sulfate heptahydrate, magnesium sulfate, and potassium nitrate.

4. **Monoclinic system:** two axes at right angles and a third at right angles to one but inclined with reference to the other. The axes may vary in relative lengths. Examples: gypsum, sodium carbonate, oxalic acid, potassium chlorate, and ferrous sulfate.

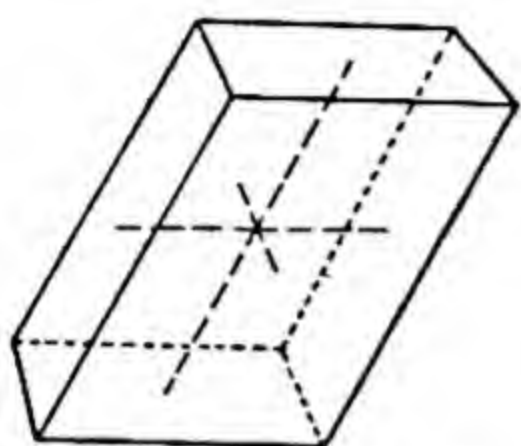


Fig. 37. Monoclinic.

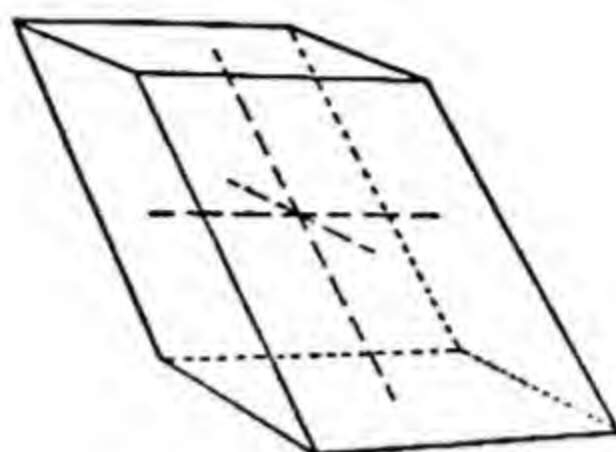


Fig. 38. Triclinic.

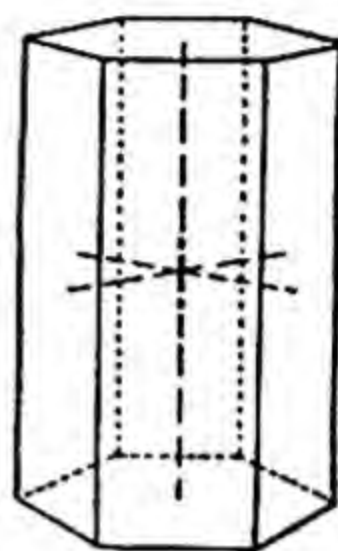


Fig. 39. Hexagonal.

5. **Triclinic system:** three axes all inclined toward each other and of any relative lengths or inclinations. Examples: calcium thiosulfate and blue vitriol.

6. **Hexagonal system:** three equal axes in the same plane intersecting at angles of 60° , and a fourth axis at right angles to all of these. Examples: quartz, sodium nitrate, beryl, and graphite.

Crystals split along definite cleavage planes. The expert who split a great rough diamond (to eliminate flaws) worth a few hundred thousand dollars studied its cleavage planes and optical axes for two months. He knew that if he aimed and struck the cutting tool incorrectly the diamond would fall into many small fragments of far less value. This man's judgment turned out to be correct — but he fainted after he struck the critical blow.

Diamonds are crystalline, but (after any necessary splitting) the facets are ground to suit the lapidary and not in agreement with the natural form of that crystal. Sulfur has two crystal forms, and an energy change is involved in a change from one to the other. When a substance crystallizes in two systems it is *dimorphous* while two or more substances crystallizing in the same form are *isomorphous*.

Crystal form may, in some instances, be influenced by the solvent from which crystallization takes place and by the presence

of other substances. Urea in salt water forces sodium chloride to crystallize in octahedra instead of the usual cubes.

In the quick-freezing of foods unusually small ice crystals are formed with less destruction of cells.

Exercise

1. Concentrate some salt water and let it stand undisturbed in an open dish. To what system do these crystals belong?

Crystal Structure. Diffraction gratings are made by ruling fine parallel lines on metal, glass, celluloid, plastics. When these lines are separated by distances approximating the wave length

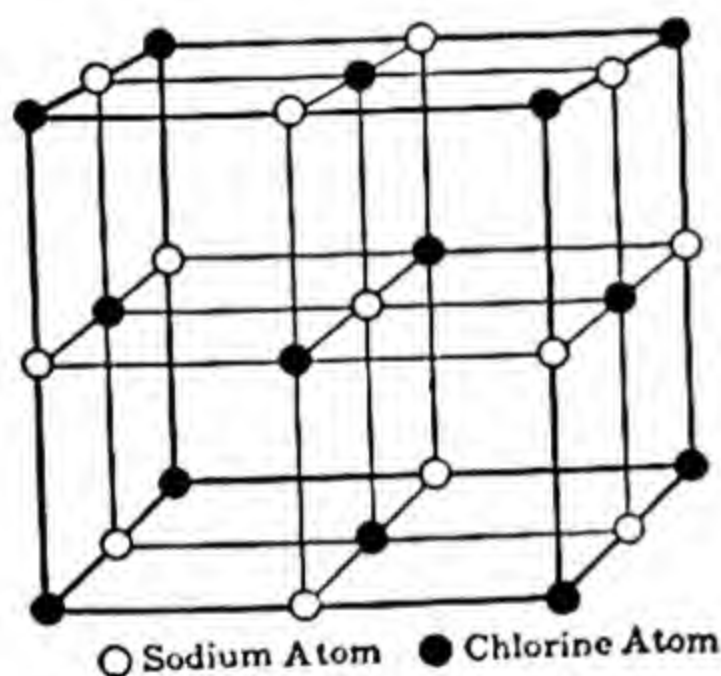


Fig. 40. Cubic arrangement of atoms in a crystal of sodium chloride.

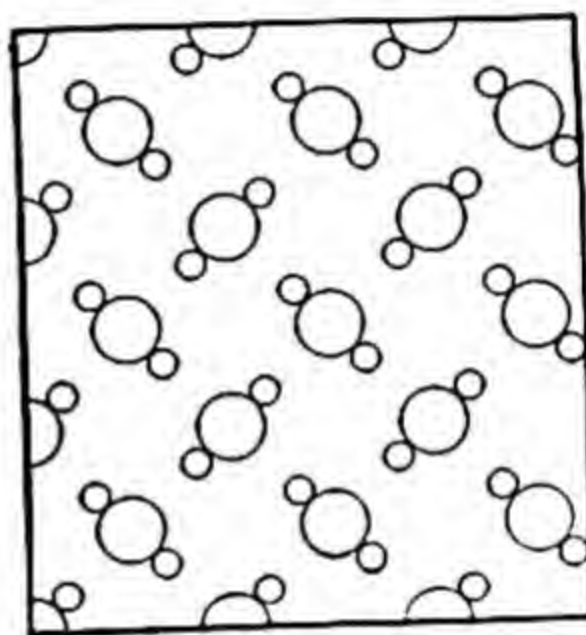


Fig. 41. Molecular space lattice in a crystalline solid. Here the molecule (not atoms) is the unit in the geometric pattern. Such a condition exists in dry ice, solid CO_2 .

of light, a spectrum is produced by incident light similar to that formed by a common glass prism. Some gratings are marked with twenty-five thousand lines to the inch (one thousand to the millimeter).

It occurred to Laue in 1912 that if these parallel lines were closer together, separated by distances of the order of X-ray wave lengths, it should be possible to secure X-ray spectra similar to those obtained with visible light. The waves in the ether known as X-rays are about one ten-thousandth the length

of light waves. To make a grating for use with X-rays there should be ruled nearly one hundred million lines to the inch — an impossibility. Laue found such gratings already prepared in crystal surfaces. Here, as Bragg pointed out in 1914, the atoms are arranged in a geometric pattern or *lattice*, giving the necessary parallel lines of atoms close enough together for Laue's needs. Later this effect of crystals on X-rays was used to determine the distance between atoms, or groups of atoms, in the crystal.

The lattice units are not single atoms in all cases. The familiar groups or radicals are found in some crystalline salts and may

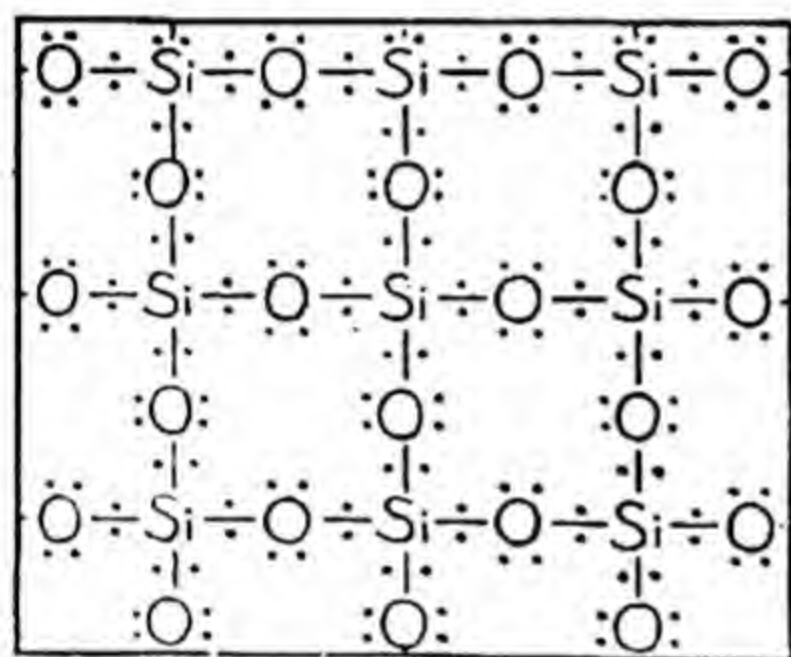


Fig. 42. Crystal pattern of silicon dioxide (SiO_2). Each silicon atom is surrounded by four oxygen atoms and each oxygen atom joins two silicon atoms. Pairs of electrons are shared between atoms so that each atom has 8 electrons around it. Such a crystal is a "giant molecule." It is very hard and does not melt readily. Courtesy: Sidney French.

is notably true with mica. X-ray photographs show that in solid carbon dioxide each carbon atom is much closer to a pair of oxygen atoms than to the other carbon atoms. In this sense the molecule, CO_2 , is a unit in the space lattice. Also, it evaporates readily from the surface of the crystals.

If a negative ion is about the same size as the surrounding positive ions more positive ions may form a group around it than if the negative ion is relatively much smaller.

carry positive or negative charges. Such charged atoms or groups are termed "ions." In calcite crystals, CaCO_3 , it was shown by X-ray examination that each carbon atom is closely surrounded by three oxygen atoms. The lattice unit of many carbon compounds (organic compounds) is the molecule, as in frozen benzene where the lattice unit is C_6H_6 .

Since the attraction between atoms in a crystal lattice varies inversely as the square of the distance, it is obvious that crystals cleave or split most readily along planes where these distances between atoms are greater than in adjoining parts of the solid. This

When a beam of X-rays is reflected from a crystal face it is found that the angle at which reflection becomes evident bears a simple relation to the wave length of the X-rays used and to the distance between adjacent layers of atoms in the crystal. The intensity of reflection from a single layer of atoms is extremely small and the reflected ray becomes appreciable only when reflections from many parallel planes of atoms are in phase and therefore reenforce each other.

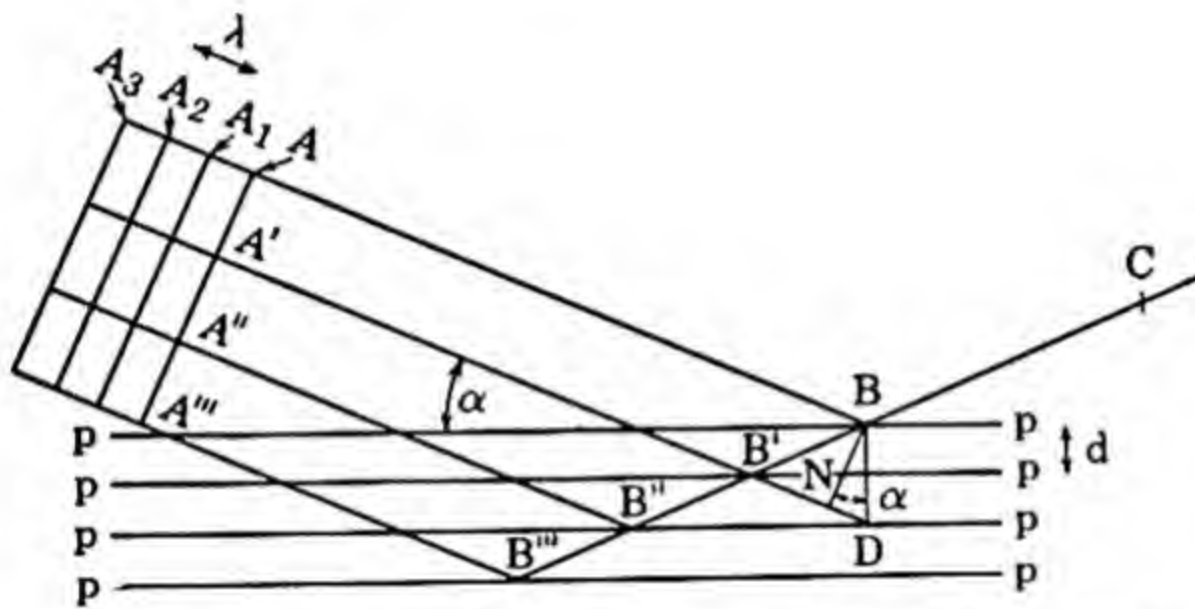


Fig. 43. Reflection of X-rays from a crystal space lattice. (Bragg).

Accordingly, the distance between adjacent planes of atoms is equal to the wave length (λ) of the X-rays divided by twice the sine of the angle of incidence (α). The wave lengths of X-rays from various sources are now quite accurately known. Therefore it is only necessary to measure the angle of incidence at which reflection occurs in order to be able to calculate the distance between adjacent planes of atoms in any crystal.

Figure 44 is a photograph of the diffraction of a fine beam of X-rays in passing through a thin crystal of silicon carbide to a photographic plate. Bragg explains that each spot is due to the regular reflection of the beam of X-rays from planes in the crystal that are especially rich in atoms.

Electron rays are now being used in crystal studies, to go farther in their revelations than is possible with X-rays. The wave lengths of the electron rays experimentally possible are only a few hundredths of one Angstrom unit, while the X-rays used in studies of crystal structure have a wave length of about one Angstrom unit.

Synthetic Optical Crystals. Large perfect crystals of sodium chloride, lithium fluoride, and a few other compounds are needed in the making of prisms and lenses for infrared spectro-

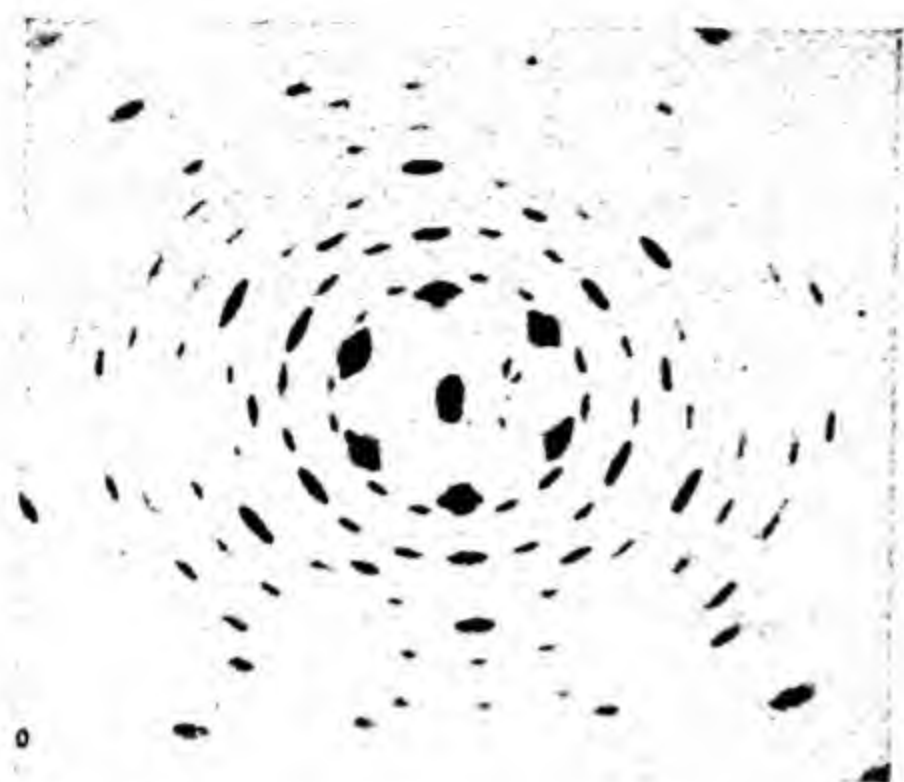


Fig. 44. X-ray photograph (Laue pattern) of a crystal of silicon carbide. (Courtesy Industrial and Engineering Chemistry).

scopes. Such crystals are formed in a platinum crucible with a 90° conical bottom. The solidification of the melted mass in the crucible begins at the tip as the crucible is slowly moved (during ten days) out of the furnace. The whole mass of several pounds is one crystal with perfect optical axes.

Electrical Effects. Certain crystals have unusual characteristics, in that when they are subjected to pressure in certain directions relative to their axes electrical charges appear on

their surfaces. Conversely, these same crystals are slightly distorted mechanically when electrical potentials are applied to the crystal faces. Such crystals are used in compact microphones in which sound pressure is converted to electrical impulses that may be amplified to any desired intensity. By a reversal of this process these crystals are used to convert electrical impulses into mechanical impulses with the advantage that a range of frequencies can be used. Perfect quartz crystals are in demand for this use.

Centered Cubes. The commonest lattice system is the face-centered (Fig. 45) with atoms at the corners of a system of equal closely packed cubes and also at the centers of each cube face.

Wyckoff¹ states that X-ray analysis has so far shown that:

1. There is no metal crystallizing in the face-centered system which is not ductile throughout a considerable range of temperature.

2. All noble metals are in the face-centered system.

¹ *Structure of Crystals*, Reinhold Publishing Corp.

3. All the best conductors of heat and electricity are in the face-centered system.

The smallest typical specimen of a crystal is the unit called a cell, such as is shown in Fig. 40. Each atom in the simple cubic crystal is surrounded by 6 of opposite kind; in the face-centered cube by 12; and in the body-centered by 8.

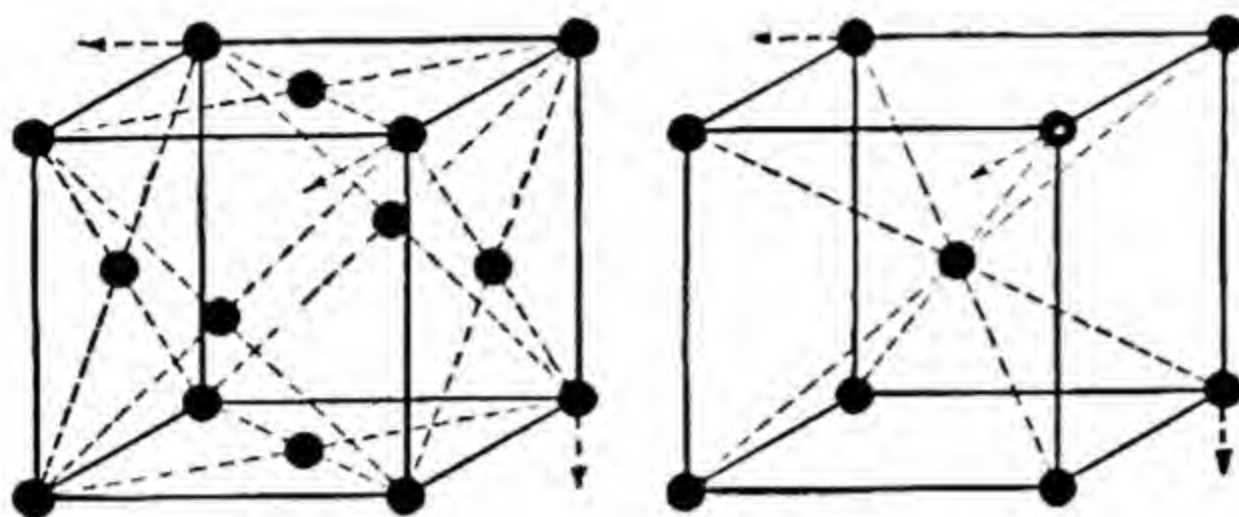


Fig. 45. Arrangements of atoms in crystals.

The ordinary crystal apparent to the eye is built up of smaller units or "cells" each having a shape typical of the crystal as a whole.

Structure of Glasses. X-ray study finds the same type of diffraction pattern for glasses as for liquids; in other words glasses and liquids are alike in their random, haphazard arrangement of

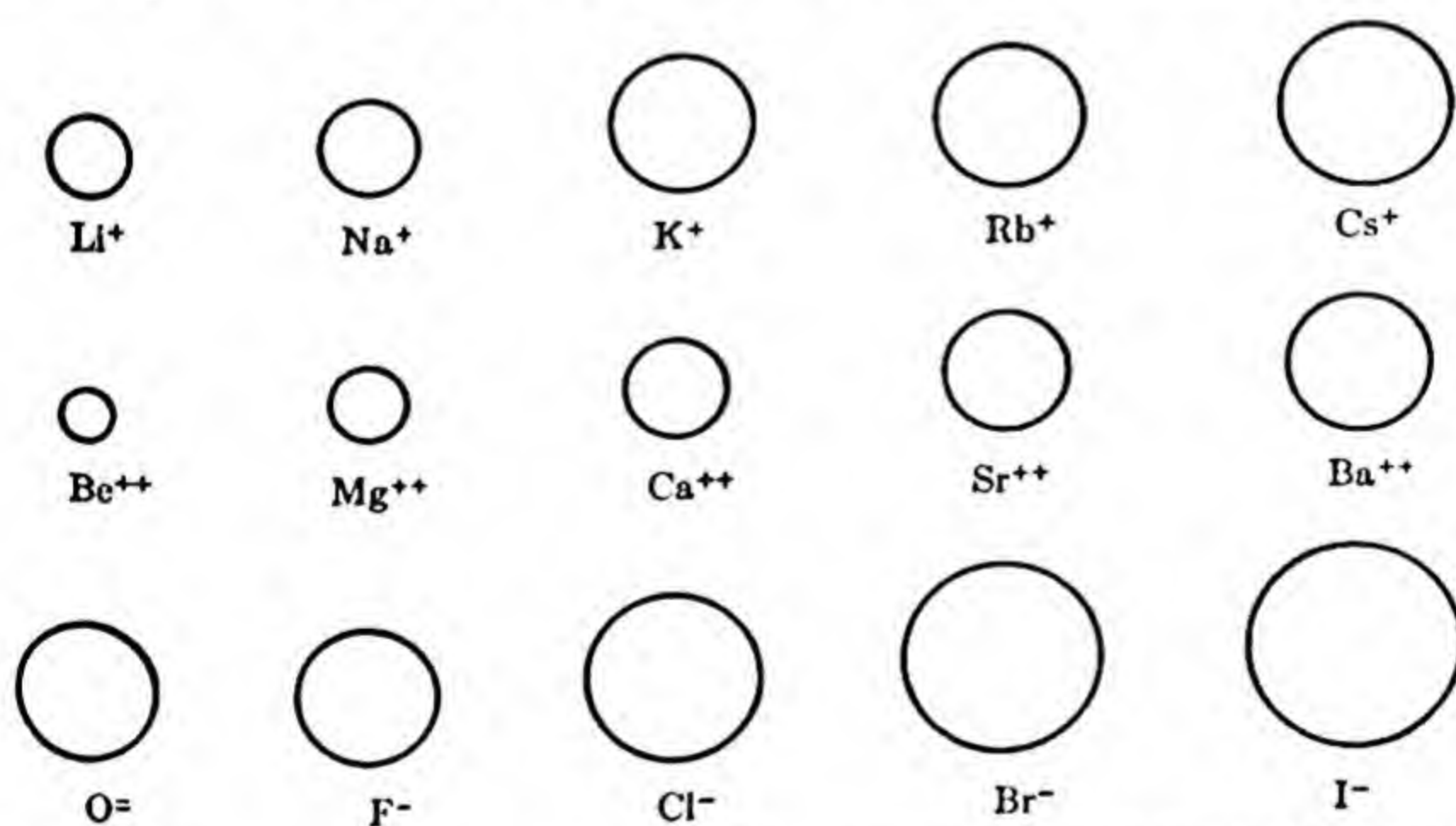


Fig. 46. Relative sizes of charged atoms (ions) in close-packed crystalline solids.

molecules or other units. Crystals possess rigidity and a definite orderly structure, while glasses possess rigidity but a random arrangement of structural units.

Exercises

2. How much heat is required to convert 350 g. of solid aluminum at its melting point into liquid aluminum at the same temperature?
3. When 680 g. of steam at 100°C . condense, cool to 0°C ., and freeze to ice, what is the total amount of heat liberated?
4. How many grams of water could be heated from 0° to 80° by the heat required to melt 12 kg. of ice at 0° ?

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- Mellor, J. W., *Comprehensive Treatise on Inorganic and Theoretical Chemistry*. London, Longmans, 1922. Vol. I, page 450: "Undercooling, Supersaturation, and Metastability."
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- Synthetic Optical Crystals*, free booklet published by the Harshaw Chemical Company, Cleveland, Ohio.

Chapter 9 HYDROGEN

History. The discovery of hydrogen is usually credited to Turquet de Mayerne (1650), who treated iron with dilute sulfuric acid and recognized the "inflammable air" formed as a distinct substance. Paracelsus had really done the same thing a century earlier but failed to recognize the "air" as a distinct substance. Cavendish in 1766 discovered many of its properties. Lavoisier named it "hydrogen," meaning "water former," although it was Cavendish who burned hydrogen in oxygen and proved that water is composed of hydrogen and oxygen.

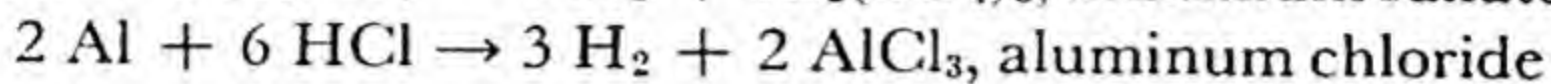
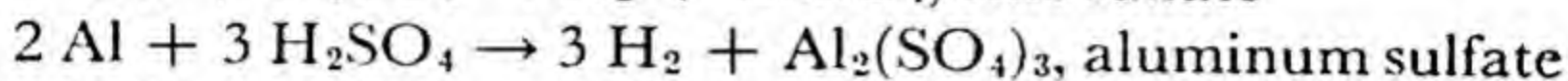
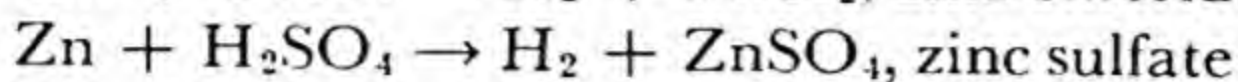
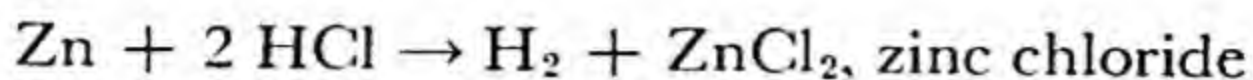
Occurrence. Hydrogen does not occur free in nature except in traces, but in the combined form it is found in water, plant and animal tissues, petroleum, asphalt, and natural gas. Among laboratory reagents we learn that it is an essential element of all acids and bases.

Gigantic flames of incandescent hydrogen and calcium 1,000,000 miles high have been known to burst from the sun's chromosphere.

Preparation: Laboratory Methods.

1. Metals and Acids. Since hydrogen is a constituent of such common materials as water, acids, and bases, these must be convenient sources for its preparation. In the laboratory it is extremely convenient to displace hydrogen from dilute acids by the

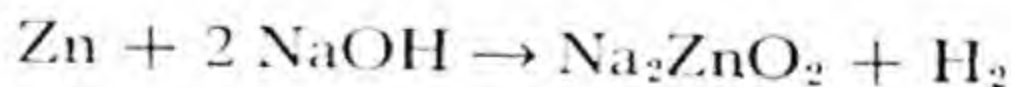
more active metals. The hydrogen is collected by displacement of water.



When a metal displaces hydrogen from an acid, a **salt** always is formed. With hydrochloric acid this salt is called a "chloride," hence ZnCl_2 is zinc chloride and NaCl is sodium chloride (common salt). With sulfuric acid the salts are called "sulfates," with nitric acid the salts are called "nitrates," and with phosphoric acid the salts are called "phosphates." The less active metals, such as copper, mercury, platinum, gold, and silver, do not displace hydrogen from acids. Some acids react more readily than others for reasons to be developed later. Pulverized metals naturally react more rapidly than do masses of metal because the greater surface allows better contact.

NOTE: A preliminary definition of acids, bases, and salts is now in order. An acid in water solution tastes sour, turns litmus paper red, and yields hydrogen when treated with the more active metals. A base in water solution feels soapy, turns litmus blue, and neutralizes the sour taste and other characteristic properties of an acid. Acids all contain hydrogen replaceable by a metal and bases all contain $-\text{OH}$ groups attached to a metal. A salt is one of the products formed when a metal displaces hydrogen from an acid (the other being hydrogen) or when an acid and a base react (the other being water).

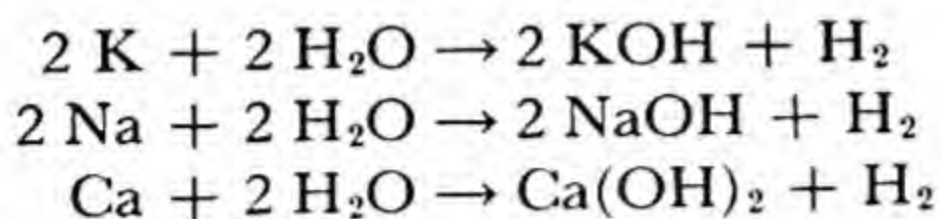
2. Metals and Bases. Several active metals displace hydrogen from bases. In some cases a warm 10 per cent solution of the base is used; in others the powdered dry metal and base are heated together:



The soluble product is called sodium zincate and the similar product of reaction between aluminum and sodium hydroxide is called sodium aluminate.

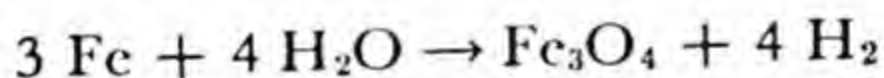
By a "10 per cent solution" we mean a solution containing 10 grams of the dissolved substance and 90 grams (or ml.) of water. Of course other weights in the same proportions may be used.

3. Metals and Water. The most active metals, such as potassium and sodium, violently displace hydrogen from cold water. In fact a bit of such a metal the size of a pea is adequate for the experiment. It is well to take due precautions, for the hydrogen is often ignited from the heat of reaction and the remaining metal melted. The globules may spatter in the careless observer's face.



Calcium acts at moderate speed. In all cases the products are hydroxides of the metals used, sodium hydroxide, NaOH, for example. It is to be noted that only half the hydrogen in each molecule of water is displaced, unless the temperature is raised considerably, no matter how much metal is used.

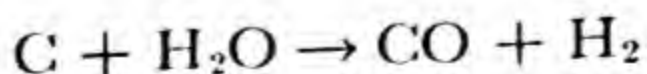
Less active metals react with water only when heated. Magnesium displaces hydrogen from boiling water if a little of an ammonium salt is present to keep the surface of the metal clean. Steam passed over red-hot iron reacts as follows:



Preparation: Industrial Methods.

4. Electrolysis. When a current of electricity is passed through water made conducting by the presence of some substance such as sulfuric acid or sodium hydroxide, we are able to collect two volumes of hydrogen at the cathode (where the current leaves) to one of oxygen at the anode (where the current enters) (Fig. 47). Since this is the exact proportion in which these gases unite to form water on burning, the experiment adds convincing proof to our ideas on the composition of water.

5. The Steam-Water Gas Method. "Water gas" is the principal source of hydrogen in the United States. Water gas itself is prepared by the process of passing steam over coke at about 1000° C.:



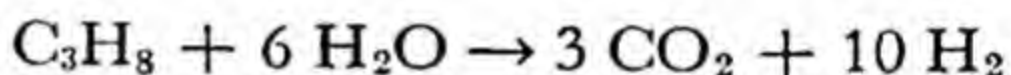
Of course, the coke is soon cooled by the steam below the reaction temperature. Steam is then shut off and a blast of air turned on. Part of the coke burns, heating the remainder up to 1000°C. , and preparing it for another blast of steam.

Water gas ($\text{H}_2 + \text{CO}$) and steam are then passed over a catalytic mixture of the oxides of iron, and chromium, at 450°C. :



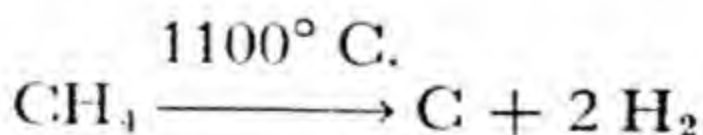
The steam oxidizes the carbon monoxide. The mixed gases are bubbled under pressure through water, which takes out the carbon dioxide. Other carbon dioxide absorbing methods are in use. This is a continuous process and very economical.

6. The Steam-Hydrocarbon Process. The very recent rise of this process to second place in hydrogen manufacture was surprising. Methane, CH_4 , in natural gas can be used, also propane, C_3H_8 from oil refineries.



The reaction proceeds at 835°C. over a nickel catalyst. Carbon dioxide is readily separated from the hydrogen.

7. The Hydrocarbon Cracking Process. Modern development of the hydrocarbon process for making hydrogen is worthy of note. Any compound of hydrogen and carbon may be broken down or "cracked" into its elements if sufficiently heated without access of air.



8. The Coal Gas Source. The coke-oven gas made from one ton of bituminous coal contains about twenty-seven pounds of free hydrogen. Low-temperature-compression liquefaction separates the other gases from hydrogen. This is a commercial source

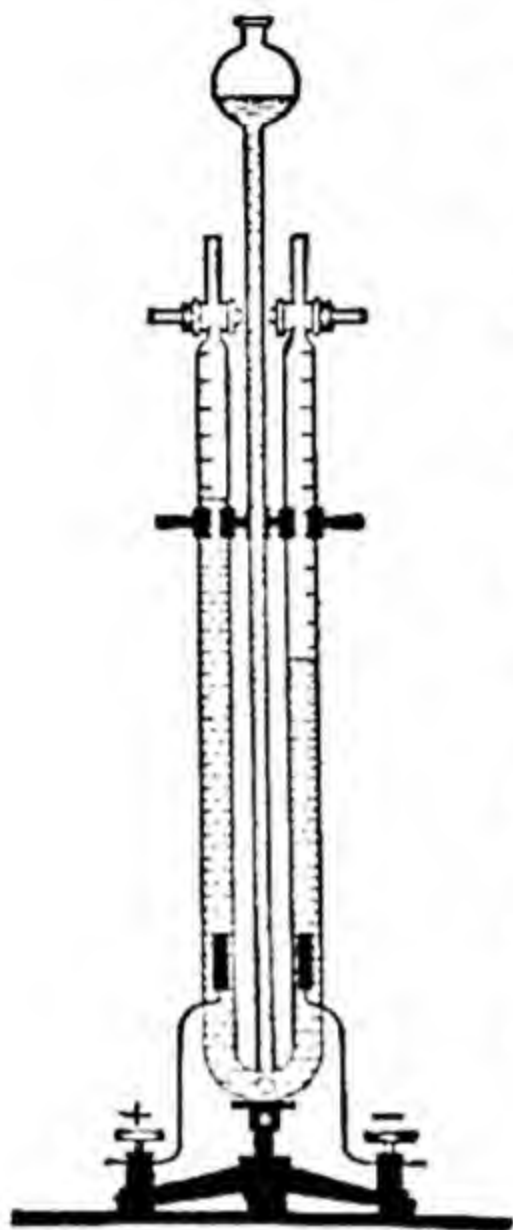


Fig. 47. Electrolysis of water.

wherever the price of coal gas is very low, as it has been in Europe.

Physical Properties. Hydrogen when pure is a colorless, odorless, tasteless gas. A liter weighs 0.08987 g. at standard conditions, so it is the lightest substance known. Liquid hydrogen looks like water, but a cork sinks in it as quickly as does a stone in water. The gas may be poured upward from cylinder to cylinder. At ordinary temperatures and 760 mm. pressure 2 ml. will dissolve in 100 ml. of water. It cannot be liquefied above $-240^{\circ}\text{C}.$, its critical temperature, where 20 atmospheres pressure are required. It has been frozen at $-257^{\circ}\text{C}.$ into a transparent, ice-like solid. Powdered palladium under favorable conditions can absorb 900 times its own volume of hydrogen, and such absorbed hydrogen is very reactive chemically. This property of dissolving in metals probably explains in part why hydrogen passes through thin sheets of hot gold, platinum, and other metals. Of course, as indicated by Graham's Law, it has the greatest speed of diffusion of all gases, and this is another factor. The loss by diffusion through balloon fabric is a serious problem.

Deuterium (Heavy Hydrogen). Several years ago it was observed that the most accurate determinations of the atomic weight of hydrogen (relative to oxygen as the usual standard) by the best chemical methods and by the most delicate physical method ("positive ray analysis," Chap. 13) failed to agree by a discrepancy of about one part in 6000. A clever observer suggested that if hydrogen contained an isotope of double the atomic weight of common hydrogen the physical method would come into perfect agreement with the chemical method. Isotopic forms of an element are alike chemically but different in the nucleus, therefore in atomic weight.

The known existence of isotopes of oxygen encouraged Urey at Columbia University to assume that if heavy hydrogen existed it might be concentrated to the point of detection, at least, by allowing a considerable quantity of liquid hydrogen to evaporate. Obviously the heavier molecules would evaporate more slowly than the lighter ones and so the last few drops of liquid should be

much richer in double-weight hydrogen. Brickwede contributed 1 ml. of residual hydrogen remaining after evaporation of about 4 liters and this was examined by Urey and by Murphy for the

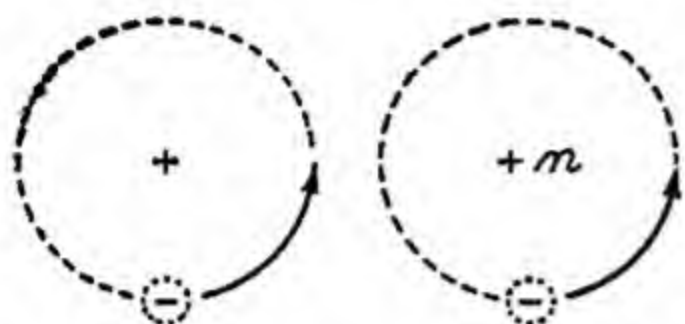


Fig. 48. Atoms of hydrogen (left) and deuterium. The nucleus of deuterium contains one free proton, and a neutron of the same mass as a proton but with no charge. There is only one planetary electron in either atom. The atomic number of both isotopes is one.

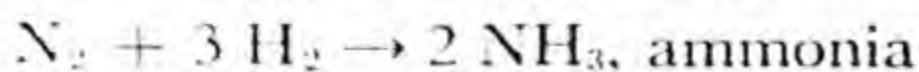
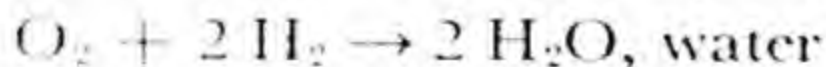
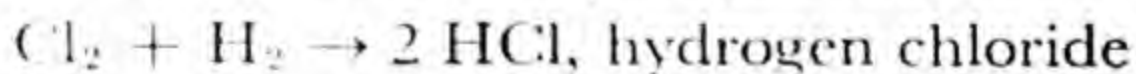
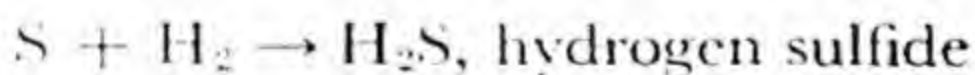
expected displacement of its spectral lines. They won, on Thanksgiving Day, 1931. Double-weight hydrogen (deuterium) was detected, but not isolated until later. The first to prepare pure "heavy water" or deuterium oxide was G. N. Lewis. One molecule out of every 6000 or more of common water is heavy water.

After some disagreement the symbol for deuterium, heavy isotopic form of hydrogen, was set down as "D" and thus the formula for heavy water as

D_2O . Of course heavy ammonia, ND_3 , is possible.

The discovery of "tritium" of atomic mass 3 has been announced. It must have one proton and two neutrons in the nucleus with one planetary electron. Like radium it is unstable, more so, in fact. Tritium is a product of the atomic pile (Chap. 27).

Chemical Properties. Hydrogen is rather inactive at ordinary temperatures, but at higher temperatures unites with most of the non-metals and many of the metals:



Hydrides, such as CaH_2 , are formed by passing hydrogen over the most active metals at elevated temperatures.

The hydrogen flame is intensely hot, because 34,195 calories are released when one gram of hydrogen burns. A special burner, called the oxyhydrogen blowpipe (Fig. 49), was devised by the pioneer American chemist, Robert Hare. This device insures

proper mixing of a stream of oxygen and a stream of hydrogen. In this flame platinum melts and silver boils. The temperature ranges from 1800° C. to 2500° C. as conditions vary.

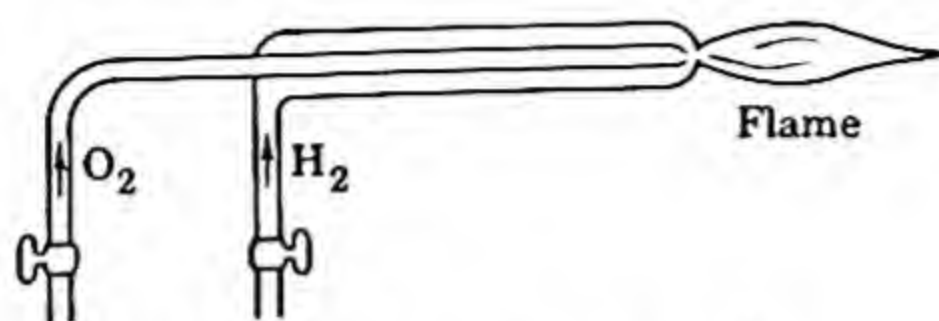
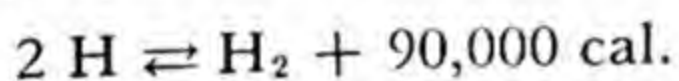


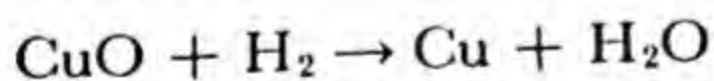
Fig. 49. Oxyhydrogen torch.

Silent erection of office buildings is possible, thanks to oxyhydrogen and oxyacetylene welding.

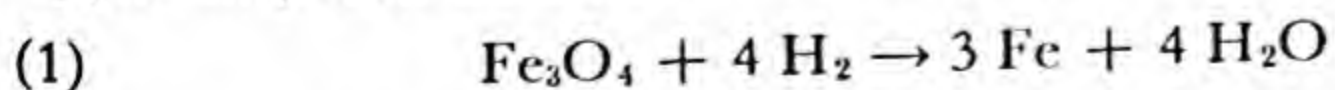
The *atomic hydrogen flame*, useful in welding thin sheets of stainless steel without oxidation, is so hot that it melts tungsten, 3370° C. A stream of molecular hydrogen passing through an electric arc absorbs energy and the energy splits the molecules into atoms. As the resulting single atoms of hydrogen unite again (out of the arc) great heat is given off:



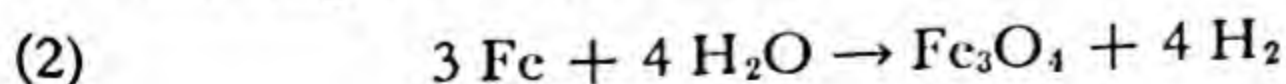
Hydrogen, when hot, removes oxygen and even some other elements from many compounds. Such a process is called *reduction*, the exact opposite of *oxidation*. However, a broader conception of reduction will soon be presented. Figure 5 (page 19) represents the reduction of heated copper oxide by dried hydrogen. The water formed is taken up by the anhydrous calcium chloride in the U tube which may be weighed.



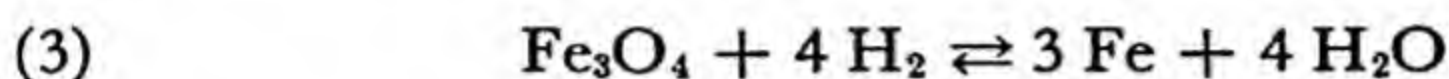
Reversible Reactions. A stream of hydrogen passed over the hot oxide of iron reduces it to the metal by stealing the oxygen. Apparently iron does not have the ability to hold its own:



If through the same tube we pass a current of steam (Fig. 50), the following reaction occurs:



The steam oxidizes the iron back to the oxide. Now if we seal iron and water in a strong closed tube and heat it for a time, we find on opening the tube all four substances — iron, hydrogen, steam, and iron oxide. Evidently when the products of reaction could not escape, both reactions took place. We express the facts thus:



and call it a *reversible reaction*. In equation (1) the steady flow of hydrogen swept the steam out of the tube before it had a fair chance to react with the iron. In equation (2) the steady flow of

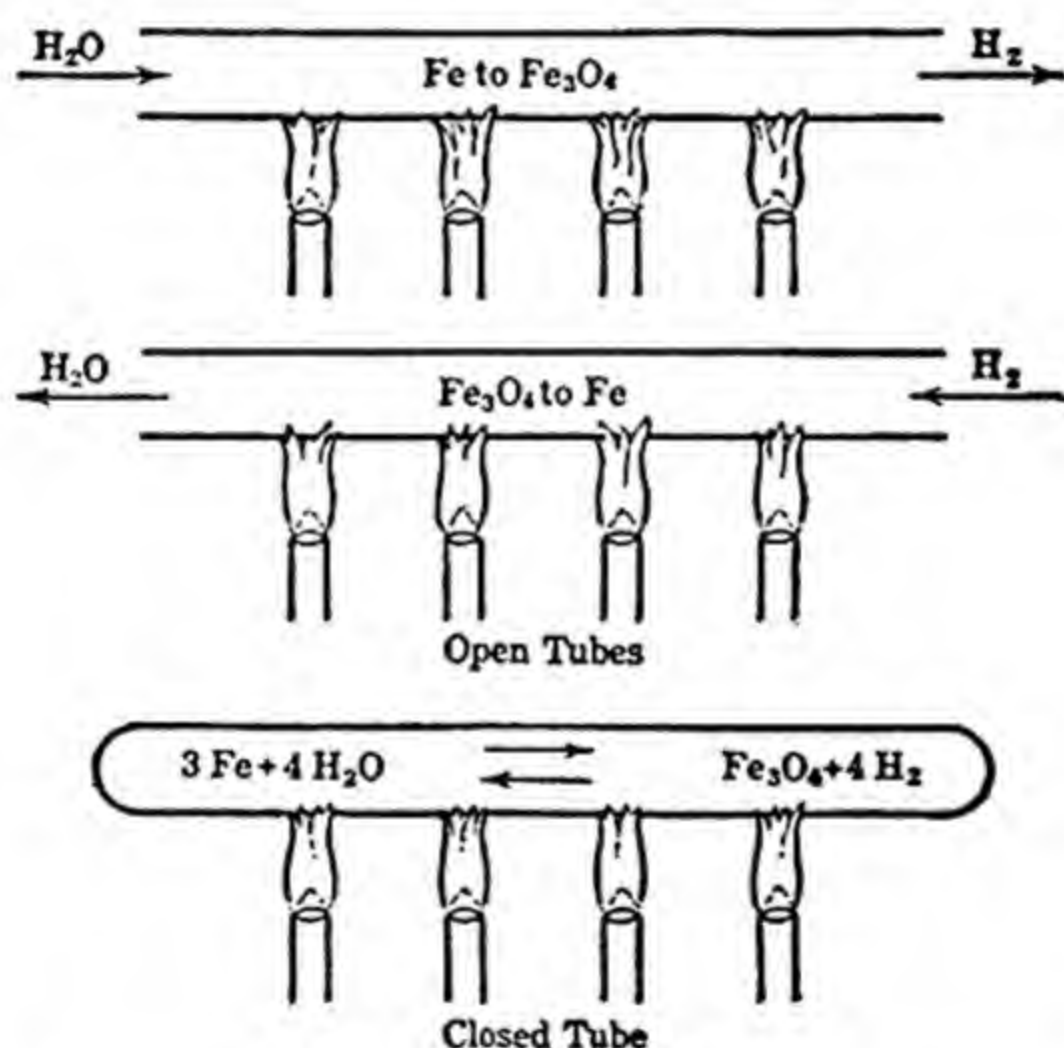


Fig. 50. Reactions in open and closed tubes.

steam swept the hydrogen out of the tube before it had a fair chance to react with the oxide. But in a closed tube every possible reaction has a chance because nothing escapes; the four substances remain in good contact.

Many reversible reactions can be made to proceed to completion by any device for removing one of the products or turning it into something inactive. The escape of a gas or the formation of an insoluble precipitate prevents reversal. There is comparatively little contact of a solution with precipitates.

In any reversible reaction like that represented by equation (3) the two opposing reactions adjust their speeds until equal; and a condition of *equilibrium* is reached when there is no further change in the relative quantities of the reacting substances. Of course any change in the conditions such as temperature, pressure, concentration, etc., will disturb this equilibrium to the right or left by favoring one reaction more than the other. A new equilibrium is soon reached.

To make the idea of equilibrium clear by the use of a rather informal illustration, let us consider the financial status of the average college student. He begins the year with a reasonable cash

reserve for emergencies, a regular allowance from home, and the expectation of certain steady expenditures, some necessary and others in the luxury class. If we consider Income and Expenditure (Outgo) as analogous to two opposing chemical reactions and the Cash Reserve as an amount that

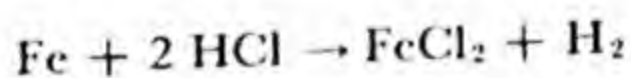


Fig. 51. Financial equilibrium.

may grow, decrease, or remain fixed (constant) as the relative velocities of Income and Outgo vary, we have a useful parallel. A healthy condition of financial equilibrium seems desirable.

Exercises

1. Why does the reaction between iron and hydrochloric acid proceed to completion although under proper conditions hydrogen reacts with the ferrous chloride formed?



2. Remembering that liquid water turns into gaseous water, that is, evaporates, give the equilibrium discussion as applied to a stoppered bottle partly filled with water.

When the stopper is removed, what happens?

Uses of Hydrogen. Hydrogen manufacture is a great industry. Hydrogen is used on the largest scale in the *manufacture of ammonia* by direct union of nitrogen and hydrogen (Haber process). Since ammonia is a starting point in the manufacture of fertilizers and of explosives, there is a great and growing demand for hydrogen. This is by far the greatest tonnage use of hydrogen.

The catalytic and high-pressure hydrogenation of petroleum to yield more gasoline is becoming a great industry. Abroad, enormous quantities of gasoline have been produced by a similar hydrogenation of lignite coal. Hydrogenation is the addition of hydrogen to certain types of molecules.

For many years hydrogen has been used in the oxyhydrogen blowtorch to weld metals or cut up large masses of scrap iron. It also has a large and growing use in hardening fats. Cottonseed oil, for example, is a liquid fat, but if hydrogen at two hundred pounds pressure is passed through it in the presence of finely divided nickel (at 175°C.), the hydrogen unites directly with the fat, forming a new substance, also a fat, but a solid. "Crisco," "Snow drift," and similar substitutes for lard are examples. Liquid fats are also hardened for use in soap making. In the United States alone nearly 1,000,000 tons of fats are hydrogenated annually.

One liter of hydrogen weighs 0.09 g., but one liter of air weighs 1.29 g. Hence the lifting power of a liter of hydrogen is the difference, or 1.2 g. under ordinary conditions.

The Montgolfier balloon was lifted by heated air (1783) while the rival balloon of Charles and Robert rose a few months later by the lifting power of hydrogen. The king of France forbade his scientists to risk their lives and decreed that useless criminals be put in the basket. Charles' eloquence overcame royal objections and the occasion became a fête with three-fourths of Paris out to see and cheer.

Some blimps still use hydrogen although helium is safer, and not flammable.

The activity series of metals represents a number of facts: the relative activity of some metals towards water; of several towards ordinary acids; and of all towards oxygen. The more active metals are placed above the less active ones.

Silver unites directly with oxygen with great difficulty; platinum and gold, not at all.

Protective films at times may confuse the student concerning the accuracy of the order of metals in the activity series. For example, aluminum and magnesium are high in activity rank yet they do not react with boiling water. This is fortunate in the kitchen. Why? Thin adherent films of oxide form and stop further attack. However, a base dissolves aluminum oxide and so

ACTIVITY SERIES OF METALS

K	Violent reaction with H ₂ O	Displace H ₂ from acids	Combine directly with oxygen
Na			
Ca	Slow reaction with H ₂ O		
Mg			
Al	Reacts with steam		
Mn			
Zn			
Cr			
Fe			
Ni			
Sn			
Pb			
H	Oxides lose oxygen when heated	Oxides (heated) of these metals easily reduced by H ₂ to free metals (and H ₂ O)	
Cu			
Bi			
Sb			
Hg			
Ag			
Pt			
Au			

gets at the metal beneath. A magnesium oxide film is removed by solutions of ammonium salts.

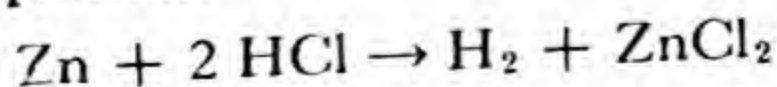
Lead is attacked by dilute sulfuric acid but the thin film of insoluble lead sulfate is so strongly adherent that the attack stops almost as soon as it starts. Because lead sulfate dissolves in concentrated sulfuric acid the action continues in the concentrated acid.

Copper, below hydrogen in the series, should not be attacked by such acids as hydrochloric or acetic, yet it is slowly attacked, in the air, because the film of copper oxide formed reacts with acids. Another oxide film slowly forms, and in turn is attacked.

How to Solve Problems. Suppose we solve a problem to illustrate an almost infallible method and compare it with the method given on page 56.

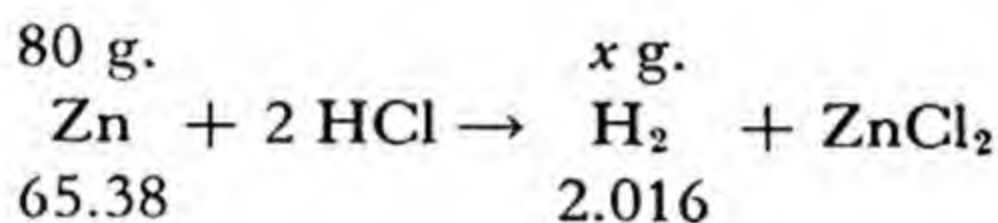
How many grams of hydrogen are formed when 80 grams of zinc react with sufficient hydrochloric acid to dissolve the metal?

1. Write the equation:



2. Select the two substances that are being discussed. From the equation we learn how many atoms or molecules are being compared. We balanced this particular equation solely to learn that one atom of zinc and two atoms of hydrogen are being compared. We are not concerned with the amount of HCl, provided there is enough to react with all the Zn, nor does the problem ask anything about the ZnCl_2 .

3. Select four numerical values relating to these two substances, two in grams (etc.) and two in terms of atomic weight units. Set the values in grams, properly labeled, above the formulas for these two substances in the balanced equation and the atomic weight values below them. Of course, x represents the unknown value:



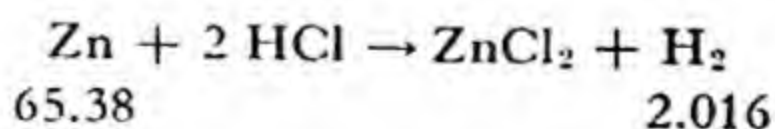
4. Write these four values in a chemical proportion exactly as indicated by step 3. Solve for x :

$$\frac{80}{65.38} = \frac{x}{2.016}$$

$$x = 2.47 \text{ grams of hydrogen}$$

If this method is followed closely, mistakes will be rare. Had liters of hydrogen been asked for, the 2.47 g. could be converted into liters after learning the weight of one liter.

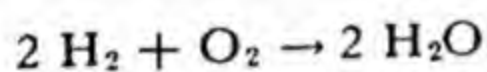
Optional Method of Solving Problems. Suppose we wish to learn how many grams of zinc will be required to displace 200 grams of hydrogen from hydrochloric acid:



It is evident from the above balanced equation that 65.38 g. of zinc displace 2.016 g. of hydrogen. Therefore to displace 1 g. of hydrogen $\frac{65.38}{2.016}$ g. of zinc will be required and to displace 200 g. there must be used $200 \times \frac{65.38}{2.016} \text{ g.} = 6486 \text{ g.}$ of zinc:

Exercises

3. What metallic oxides are readily reduced to metal by hot hydrogen?
4. How is a "salt" formed? Name a few.
5. What is the "water gas" method of preparing hydrogen?
6. Name four elements with which hydrogen unites directly on heating. What metals displace hydrogen from cold water? From hot water or steam? From dilute acids? What metals do not displace hydrogen from dilute acids?
7. If you heated potassium chlorate in a strong closed tube, would the reaction be reversible?
8. How can you change liquid cottonseed oil ("Wesson oil") into a fat having the consistency of lard?
9. When a proper mixture of hydrogen and oxygen is ignited, a sharp explosion occurs. The pressure generated may even burst the containing vessel. Since fewer molecules exist than before



how can you account for the increase in pressure?

10. Seventy liters of hydrogen (standard conditions) are passed through a heated tube containing dry copper oxide. What weight of water could be condensed beyond the heated tube?
11. How many liters of hydrogen (measured under standard conditions) can be released from water by 24 g. of calcium?
12. How many grams of iron will be required to release 150 g. of hydrogen from sulfuric acid?
13. How many grams of sulfuric acid will exactly react with 200 g. of aluminum?
14. Will silver react with hydrochloric acid?
15. Calculate the percentage of oxygen in potassium chlorate.
16. How many grams of oxygen are in 4.3 kg. of potassium chlorate?
17. Hydrogen was passed over heated copper oxide. The water formed was collected and found to weigh 80 g. (a) What is the weight of the hydrogen that reacted with the copper oxide? (b) What is the loss in weight of the CuO?

NOTE: Unless otherwise stated volumes of gases will always refer to standard conditions of temperature and pressure.

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- Urey, H. C., "Significance of the Hydrogen Isotopes." *Ind. Eng. Chem.* 26, 803 (1934).
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Chapter Outline

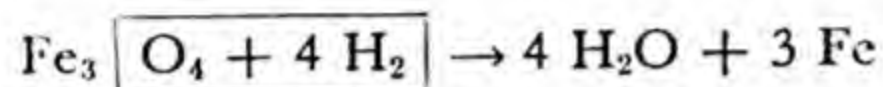
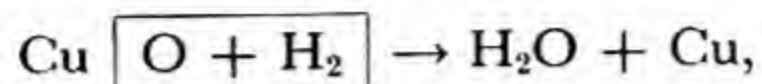
1. History of Hydrogen.
2. Occurrence.
3. Preparation
 - from acids,
 - from bases,
 - from water,
 - by certain metals (cold or hot),
 - by carbon,
 - by electrolysis,
 - from water gas,
 - from coke oven gas,
 - by cracking hydrocarbons,
 - by cracking ammonia.
4. Physical Properties.
5. Deuterium.
6. Chemical Properties of Hydrogen
 - What reactions proceed with cold molecular hydrogen?
 - What reactions proceed with hot molecular hydrogen?
 - What reactions proceed with hydrogen aided by catalysts?
 - What reactions proceed with atomic hydrogen?
7. Reversible Reactions
 - Name a reaction which you can drive to right or left as you wish or maintain at a definite equilibrium as you desire.
 - How is it managed?
8. Uses of Hydrogen.
9. How Is Atomic Hydrogen Made and Used?
10. Activity Series.

Review Suggestions

Ten minutes' questioning of yourself on the things brought out in the lecture, if given within two hours, is worth an hour's review the next day.

In all equations underline the formulas for insoluble products. Use an arrow pointing upward (\uparrow) to indicate the escape of gases formed.

In writing equations it tends toward clearness to "fence in" the elements that you know from laboratory observation must unite.



Chapter 10 VALENCE

Valence is most easily understood by reasoning from experiment. (The electronic explanation is given later in this chapter.) If we weigh out the metals sodium, magnesium, and aluminum in proportion to their atomic weights, we should take 23 g. Na, 24 g. Mg, and 27 g. Al. For that matter 23 tons Na, 24 tons Mg, and 27 tons Al would maintain the same proportion. As a matter of convenience it is better to weigh out 23 mg. Na, etc. The relative weights of single atoms have been determined on a basis of

comparison with the oxygen atom as of atomic weight 16.

It is of vital importance here to know that a "gram-atomic weight" of sodium (23 g.), a gram-atomic weight of magnesium (24 g.), and a gram-atomic weight of aluminum (27 g.) each contain the same number of atoms. If this is not clear, imagine that French soldiers average 150 lb. and German soldiers 160 lb. Calculate the number of sol-

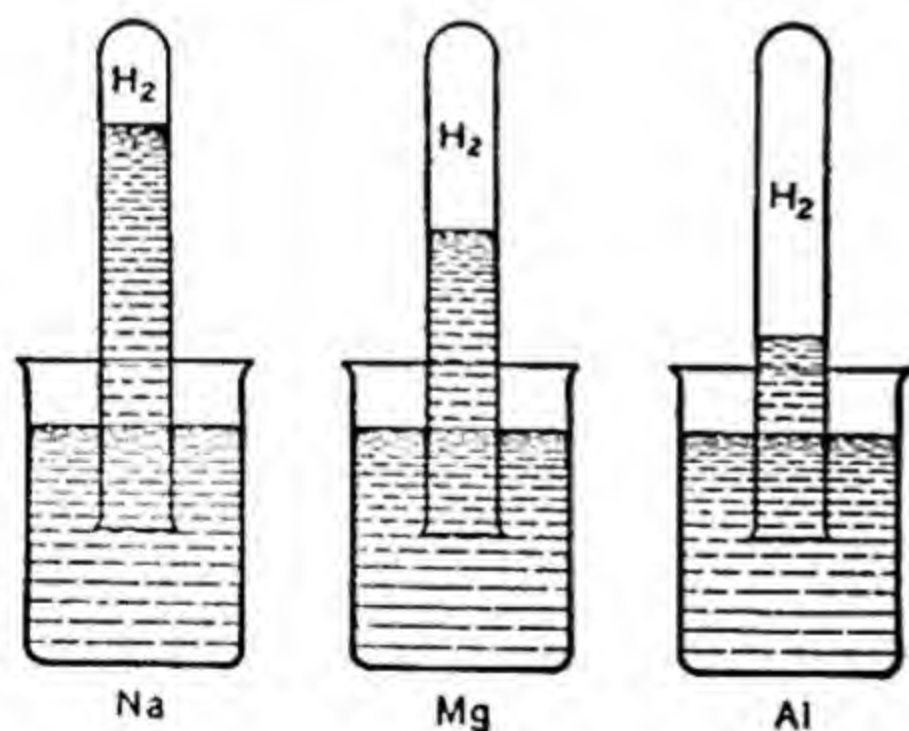


Fig. 52. Relative volumes of hydrogen displaced by milligram atomic weights of sodium, magnesium, and aluminum.

diers in a detachment of Germans with a total weight of 160,000 lb. and in a detachment of French soldiers with a total weight of 150,000 lb. Evidently there are 1000 men in each

detachment. We weighed out both groups in proportion to the weights of the individuals.

Suppose, then, that we weigh out 23 mg. of sodium,¹ 24 mg. of magnesium, and 27 mg. of aluminum and introduce them under inverted tubes of dilute hydrochloric acid (a solution of HCl in water). In laboratory practice the tubes may rest in submerged crucibles containing the metals. After the hydrogen released has displaced water from the tubes into the beaker of water below, the tubes are adjusted until the levels of water inside and out are the same. Making the usual corrections for pressure, temperature, and presence of water vapor, the results are as follows:

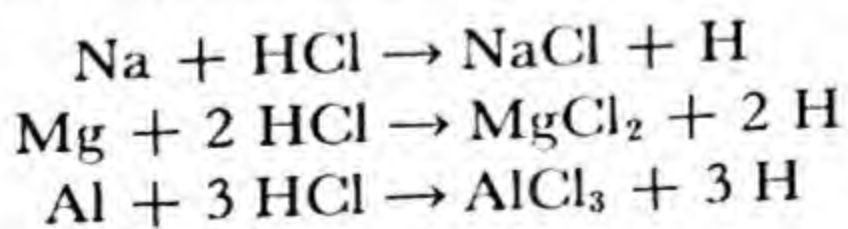
23 mg. sodium	release 11 ml. hydrogen = 1 mg.
24 mg. magnesium	release 22 ml. hydrogen = 2 mg.
27 mg. aluminum	release 33 ml. hydrogen = 3 mg.

(From the weight of 1000 ml. of hydrogen, 0.09 g., the weight of 11 ml. can be calculated by proportion.)

From the above results we see that one atomic weight of sodium *in milligrams* releases exactly *one* atomic weight of hydrogen in milligrams, while one atomic weight of magnesium in milligrams releases *two* atomic weights of hydrogen in milligrams, and one atomic weight of aluminum in milligrams releases *three* atomic weights of hydrogen in milligrams.

By using the *atomic weight* of each metal in milligrams we knew we were using equal numbers of atoms. The above results can then be expressed as:

1 atom of sodium	displaces 1 atom of hydrogen
1 atom of magnesium	displaces 2 atoms of hydrogen
1 atom of aluminum	displaces 3 atoms of hydrogen



¹ In practice it is best to put the fresh-cut sodium in a small gelatin capsule. In a few minutes the capsule is dissolved and the water comes in contact with the sodium. Magnesium ribbon should be cleaned with sandpaper, and aluminum etched with dilute base, washed, and dried before weighing.

Not merely does one atom of sodium displace one atom of hydrogen, but in the resulting compound, sodium chloride, it *holds* one atom of chlorine, that is, it is equivalent to it in holding capacity just as 1 Cl is equivalent (for chemical reaction purposes) to 1 H. Furthermore, one atom of hydrogen *holds* one atom of chlorine in a molecule of hydrogen chloride (HCl). We see that the displacing capacity (towards hydrogen) and the holding capacity (towards chlorine) are twice as great with magnesium and three times as great with aluminum as with sodium. *Valence is a number which indicates how many atoms of hydrogen or chlorine one atom of a given element will displace or hold.* One atom of a monovalent element displaces or holds one atom of hydrogen or holds or displaces one atom of chlorine. Of course one atom of a divalent element could displace two atoms of hydrogen or hold two atoms of chlorine. Magnesium must be divalent and aluminum trivalent. Oxygen, as shown by the formula H_2O , must have a valence number of two, since one atom holds two atoms of monovalent hydrogen. CaO is the accepted formula for quicklime, calcium oxide. Since we have just reasoned that the valence number of oxygen is two, we now have a logical right to state that the valence number of calcium is also two, for one atom of calcium holds one atom of divalent oxygen. A common error at this point is the incorrect statement that any *element* one atom of which holds just one atom of any other element is monovalent. Some chemists prefer to define valence as the number of gram-atomic weights of hydrogen that one gram-atomic weight of the element will displace or hold.

$$\frac{\text{Exact atomic weight}}{\text{Equivalent weight}} = \text{valence number}$$

or, exact atomic weight = valence number \times equivalent weight.
(Equivalent weight and combining weight are the same.)

Exercise

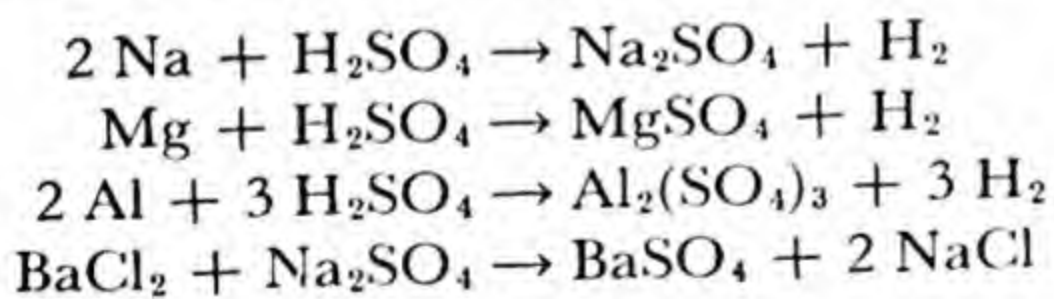
1. According to the formulas HCl , H_2O , NH_3 , and CH_4 , what do we know of the valence numbers of chlorine, oxygen, nitrogen, and carbon?

We have just learned by experiment that the valence number of aluminum is three. And since oxygen is divalent, the correct formula for aluminum oxide must be Al_2O_3 . The total valence numbers of the two aluminum atoms is six, which equals, as it should, the total valence numbers, six, of the three oxygen atoms.

2. What must be the correct formula of magnesium oxide? Of calcium chloride? Of sodium oxide?

Some elements have two or more valence numbers, but most have only one. In red cuprous oxide, Cu_2O , the copper is monovalent, for it takes two atoms of it to hold one divalent oxygen atom. In black cupric oxide, CuO , the copper is divalent, for one atom holds one atom of divalent oxygen. In the two chlorides of iron, FeCl_2 and FeCl_3 , ferrous and ferric chlorides, we have another illustration of variable valence. Nitrogen in its five oxides, N_2O , NO , N_2O_3 , NO_2 , N_2O_5 , shows different valence numbers. But when an element has more than one valence number, it is well to remember that in most cases only one is common. The usual valence number of copper is two.

Radicals. We have already noticed in equations, such as



that one sulfur atom and four oxygen atoms seem to hold together as a group or *radical* during reactions, passing from one compound to another unchanged, much as a family of Arabs might move from one tribe to another without the loss of any of its units, parents or children. We call the SO_4 group of atoms the "sulfate radical." It is incapable of existing free and its compounds are always called "sulfates." For example, H_2SO_4 is always known as "sulfuric acid," but it can be called "hydrogen sulfate." Sodium sulfate is Na_2SO_4 , magnesium sulfate is MgSO_4 , and aluminum sulfate is $\text{Al}_2(\text{SO}_4)_3$. In nitric acid, HNO_3 , and the nitrates derived from it such as NaNO_3 and $\text{Cu}(\text{NO}_3)_2$, we find the NO_3

group of atoms holding together pretty well through certain reactions, so we call it the "nitrate radical." In phosphoric acid, H_3PO_4 , and the phosphates made from it, such as Na_3PO_4 , we see a similar group — PO_4 — called the "phosphate radical." In HNO_3 a single nitrate radical holds one monovalent hydrogen; in H_2SO_4 the sulfate radical plainly holds two hydrogens; in H_3PO_4 the phosphate radical holds three hydrogens. The natural assumption is that the nitrate radical is monovalent, the sulfate radical divalent, and the phosphate radical trivalent. We can easily learn the valence number of any acid radical by looking up the correct formula of the corresponding acid and counting the hydrogen atoms held by one radical. A knowledge of the valence numbers of radicals is very convenient in remembering correct formulas. For example, CuSO_4 must be the correct formula for copper sulfate because we know already that copper is divalent (see CuO) and so is the sulfate radical (see H_2SO_4). Therefore the two valence numbers just exactly balance each other, as they

COMMON VALENCE NUMBERS

		MONOVALENT	DIVALENT		TRIVALENT	
METALS	Sodium	Na^+	Calcium	Ca^{++}	Aluminum	Al^{+++}
	Potassium	K^+	Copper (ic)	Cu^{++}	Iron (ferric)	Fe^{+++}
	Ammonium	NH_4^+	Magnesium	Mg^{++}	Chromium	Cr^{+++}
	Silver	Ag^+	Mercuric	Hg^{++}	Arsenic	As^{+++}
	Mercurous	Hg^+	Iron (ferrous)	Fe^{++}	Antimony	Sb^{+++}
		or Hg_2^{++}	Lead	Pb^{++}		
NON-METALS			Zinc	Zn^{++}		
	Chlorine	Cl^-	Oxygen	O^{--}	Nitrogen	N^{---}
	Bromine	Br^-	Sulfur	S^{--}	Phosphorus	P^{---}
	Iodine	I^-				
RADICALS	Fluorine	F^-				
	Hydroxide	OH^-	Carbonate	CO_3^{--}	Phosphate	PO_4^{---}
	Nitrate	NO_3^-	Sulfate	SO_4^{--}	Arsenate	AsO_4^{---}
	Chlorate	ClO_3^-	Sulfite	SO_3^{--}		
	Bicarbonate	HCO_3^-				

Tetravalent carbon and tetravalent silicon may be added to this table. Sulfur, nitrogen, phosphorus and arsenic also have other valence numbers than those assigned in the table.

should in all compounds. $\text{Al}_2(\text{SO}_4)_3$ must be the correct formula for aluminum sulfate because the valence number of aluminum is three (see AlCl_3) and of the sulfate radical two. Consequently AlSO_4 cannot be right, because a valence number of three for the metal is not equal to a valence number of two for the radical. Two aluminum atoms furnish a total of six (2×3), just equaled by the total six (3×2) of the three sulfate radicals. It is a great help to put marks above the elements or radicals, as in $\text{Ca}''\text{Cl}_2$ or $\text{Al}_2'''(\text{SO}_4)_3''$ or $\text{Cu}''(\text{NO}_3)_2$, to indicate their valence.

3. With the help of the above valence table write the correct formulas for zinc nitrate, cupric bromide, carbon tetrachloride, carbon dioxide, silicon dioxide, barium sulfate, and a simple compound of hydrogen and carbon.
4. If 65.4 mg. of zinc displace 22 ml. of hydrogen from some acid, what must be the valence numbers of zinc? Deduce this from the valence experiment at the beginning of the chapter.
5. Since CaO is the correct formula for calcium oxide (quicklime), what must be the formula for calcium bromide? From the formula BaCl_2 for barium chloride deduce the correct formula for barium sulfate.

CHART OF COMPOUNDS

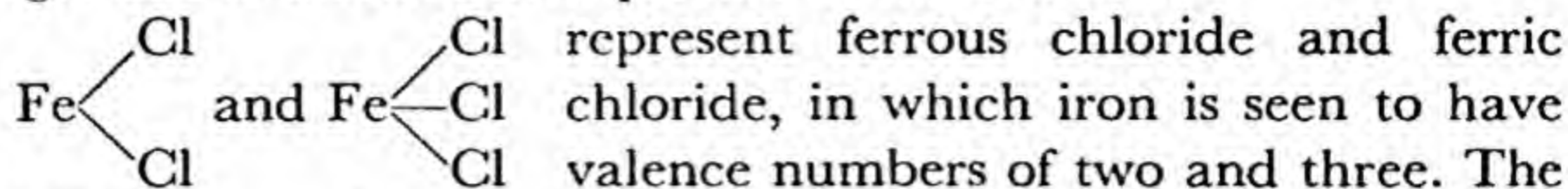
Fill in with correct formulas

	Cl	(NO ₃)	(OH)	O	S	(SO ₄)	(CO ₃)	(PO ₄)
H								
Na								
K								
Ca							CaCO_3	
Mg								
Fe''								
Fe'''								
Al								
Cu								$\text{Cu}_3(\text{PO}_4)_2$
Ag					Ag_2S			

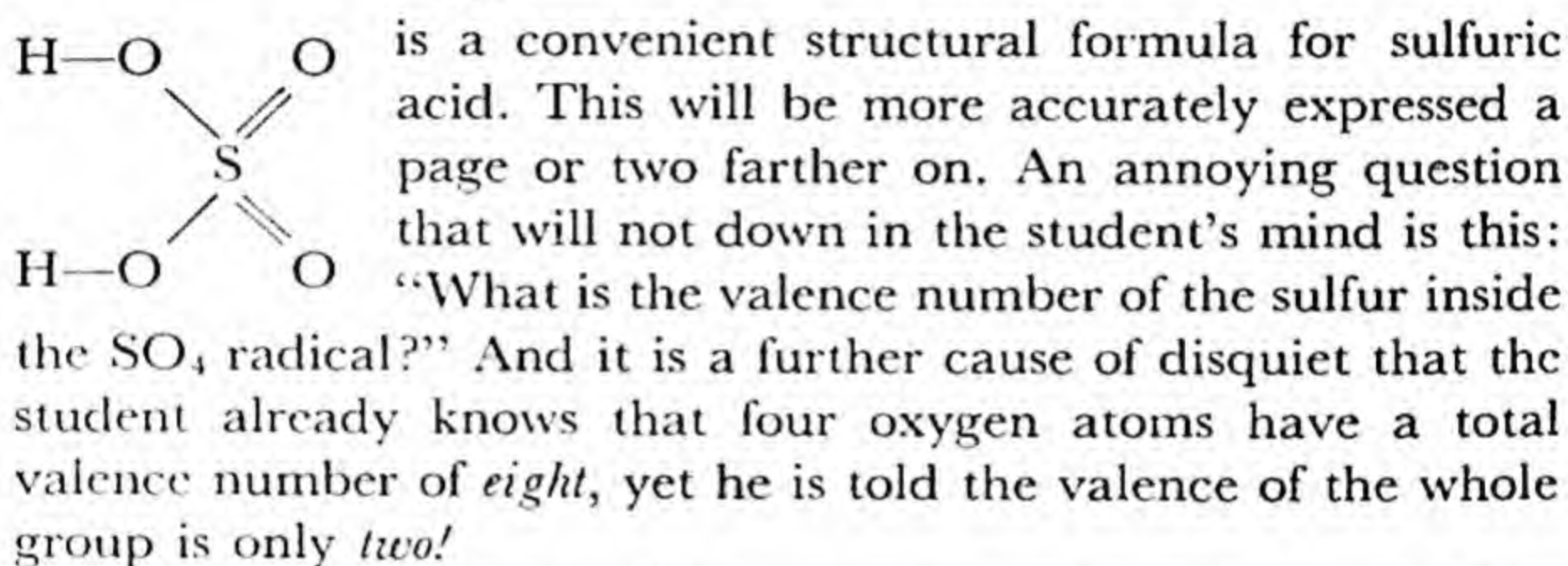
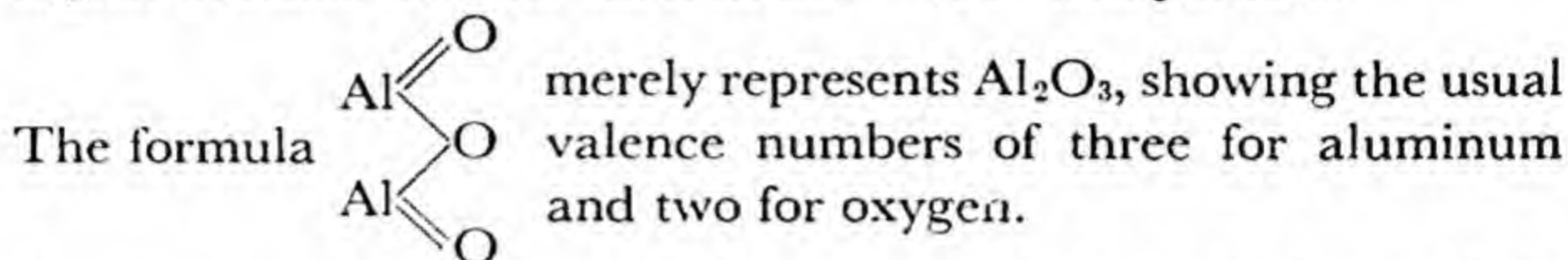
Hand in a copy of your completed chart.

Structural Formulas. It is convenient, although wholly diagrammatic, to represent the valence units between elements by straight lines or "bonds of valence." Thus Na—Cl is the structural formula for sodium chloride (common salt). Since the

valence number of sodium as well as that of chlorine is one, this single line is a convenient picture of the relation.



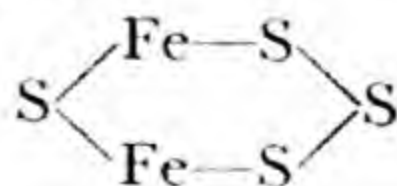
“-ic” compounds of a metal are those in which the metal has a higher valence number than in the “-ous” compounds.



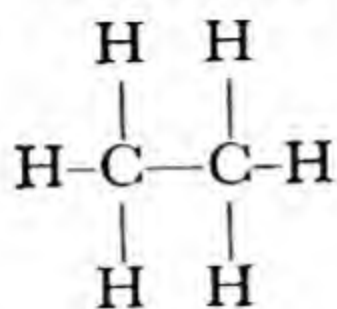
A glance at the structural formula of sulfuric acid shows us that the sulfur atom and the four oxygen atoms of the SO_4 radical are well occupied in holding each other. The effective outside valence number toward hydrogen or other atoms is only two.

The valence number of iron in Fe_3O_4 is not apparent until the formula is written as $\text{FeO} \cdot \text{Fe}_2\text{O}_3$ which shows that both divalent and trivalent iron atoms occur in the molecule.

The structural formula of black ferrous sulfide, FeS , is evidently $\text{Fe}=\text{S}$ but that of the yellow mineral iron pyrites, Fe_2S_4 , is not so simple. Perhaps it is



In ethane, C_2H_6 , the valence of carbon might seem to be three, yet if the structural formula is written it is seen that each carbon is holding the other and that the correct valence number of carbon is four:



Electrovalence. When sodium unites with chlorine to form molecules of sodium chloride, the sodium atom really loses an electron to the chlorine atom (p. 27). This leaves an excess of *one* positive charge on the sodium atom — and in the compound formed the valence number of the sodium atom is *one*, a *positive* valence of one. When the neutral chlorine atom gains an electron, it possesses an excess of *one* negative charge — and in the compound has a *negative* valence number of one. (These charged atoms are called “ions.”) The bond between atoms set up by electron transfer is called an electrovalent bond. It is limited to acids, bases, and salts although these compounds may also use covalent bonds.

Covalence. In many reactions electrons are not transferred but shared in pairs by two atoms. Each atom contributes one electron to make a pair by which the two atoms are held together with a valence of 1. If the valence number of each atom is 2 it is necessary that two pairs be shared.

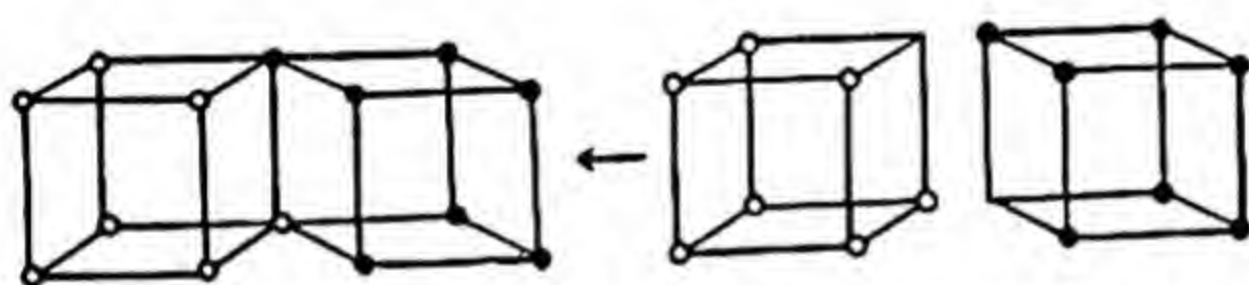
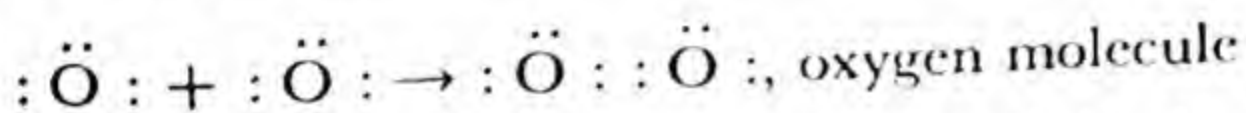


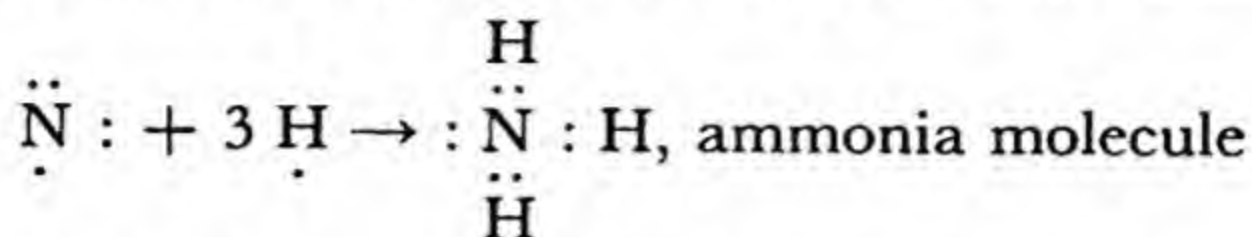
Fig. 53. A molecule of fluorine formed from two atoms by the sharing of one pair of electrons.

If dots be used to represent all the valence electrons of the outer shell or layer and two dots (:) to represent a covalent bond of 1, the following valence formulas will be understood:



Here two oxygen atoms with six electrons each in the outer or valence layer of electrons (inner layer not represented here) unite

by sharing two pairs of electrons to form a molecule, O_2 , in which each has a claim on eight electrons for its outer shell.



Here a nitrogen atom with five outer valence electrons unites by covalence with three atoms of hydrogen each of which con-

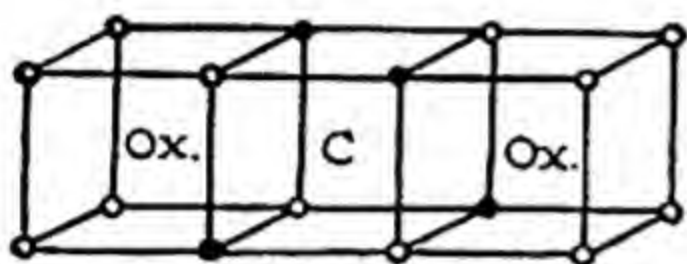
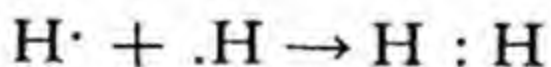


Fig. 54. A non-polar molecule of carbon dioxide formed by sharing two pairs of electrons.

tributes one electron for the three electron pairs necessary. There is no transfer of electrons, merely the formation of a covalent compound, ammonia, in which nitrogen has a claim on eight electrons for its outer shell.

It is probable that these shared pairs of electrons are attracted more powerfully by the positive nucleus of the smaller atom than by the other, thus making one of the atoms seem more negative than the other.

As a matter of fact electron pairs are shared equally only in the case of identical atoms (or groups) where the atomic radii are equal:



It is really not a simple matter in covalent compounds to call one element positive when it has not lost electrons and another negative when it has not gained electrons. For convenience we usually call the metals positive for they are more likely to lose electrons than are the non-metals. Liquid HCl is a non-conductor because of the covalent linkage (unlike electrovalent $NaCl$). However, a water solution of HCl shows the presence of H^+ and Cl^- ions.

This ionizing effect of water on covalent HCl is due to the great attraction of water molecules for the proton (H^+), a hydrogen atom minus its planetary electron. Solvents such as benzene (C_6H_6) have no such proton attraction. A solution of HCl gas in benzene does not attack marble, unlike ordinary hydrochloric acid.

The atoms inside a radical (NO_3^- , $\text{SO}_4^{=}$, $\text{CO}_3^{=}$, etc.) are held together by covalent bonds.

In dilute solutions the actual condition of H_2SO_4 is best indicated by $\text{H}^+ \left[\begin{array}{c} : \ddot{\text{O}} : \\ : \ddot{\text{O}} : \ddot{\text{S}} : \ddot{\text{O}} : \\ : \ddot{\text{O}} : \end{array} \right] =$ where hydrogen atoms are attracted by electrovalence while oxygen atoms are held to the sulfur by covalence.

The H^+ refers to a hydrogen atom which has given its electron to another atom. After the loss H^+ is called a *hydrogen ion* (charged atom or group of atoms). The $\text{SO}_4^{=}$ group in brackets has gained two electrons, becoming a divalent negative ion.

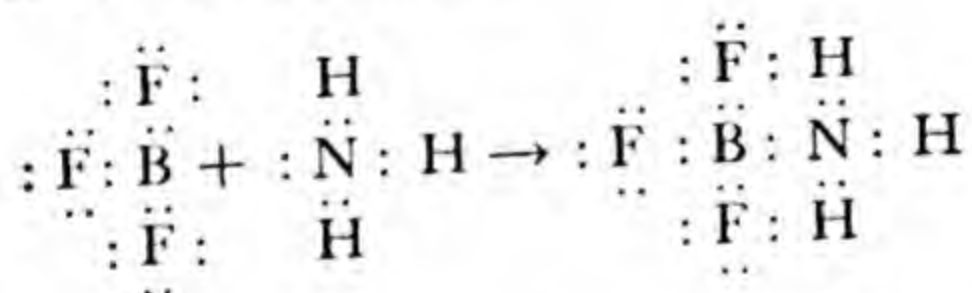
Anhydrous ferric chloride has a low boiling point, is soluble in the hydrocarbon solvents, and is a poor conductor in the fused state. All this is connected with covalent linkage. Ferric chloride reacts with water (as does HCl) to form electrovalent bonds with resulting high conductivity.

Evidently a shift of the electron pair in covalent compounds may be influenced by the solvent.

The two electrons in a covalent bond spin in opposite directions, thus setting up an electromagnetic force drawing the atoms together.

Coordinate Covalence. When both electrons in a shared pair come from one atom the valence bond relates to coordinate covalence.

Two molecules of different substances may unite by coordinate covalence. For example,



represents the union of boron trifluoride with ammonia. Note that the boron atom lacks two electrons of completing an outer shell of eight. Nitrogen, with a free pair, donates the joint use of this pair to the boron to form the coordinate bond.

Positive and Negative Valence Numbers. Electrically neutral atoms have no valence number. It is only in compounds, after electrons have been given away or taken up, or shared, that atoms exercise valence. An element such as a metal or hydrogen

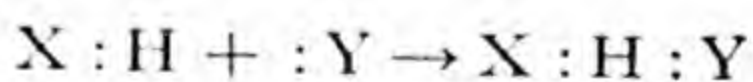
that has given away one electron has a positive valence number of one; if it has given away two electrons, it has a positive valence number of two. An element that has gained one electron has a negative valence number of one; if it has gained two electrons, it has a negative valence number of two.

In any compound the algebraic sum of the positive and negative valence numbers is zero. Thus in H_2O the total positive valence of the two hydrogen atoms is two and the negative valence of the oxygen atom is also two.

In compounds of one non-metal with another, the more active element is usually said to exhibit a negative valence. For example, in PCl_3 the chlorine has a negative valence number of one and phosphorus a positive valence number of three.

An element may be positive towards one element and negative towards another as with sulfur in SO_2 and H_2S . In covalent sharing the pair of electrons is nearer the positive nucleus of the smaller atom.

Hydrogen Bridges. The valence number of an atom is not always the same as the number of bonds connecting it to other atoms. "Until recently," states M. L. Huggins, "it has not been generally realized that a hydrogen atom already bonded to one other atom can, under certain circumstances, become bonded to a second atom in the following way:



Hydrogen forms strong bridges or bonds like the above between a few atoms such as O, F, N and much weaker bridges or links between some others. A *hydrogen bridge* is roughly one-tenth as strong as an ordinary single bond in an organic molecule.

In ice, each oxygen atom is held to four neighbors through hydrogen bridges. In liquid water these bridge connections (due to heat motions of the molecules) are continually being broken and new ones formed. Many loose molecular compounds may be attributed to hydrogen bridge formation.

Oxidation and Reduction in Terms of Electrons. Although the original conception of oxidation meant the addition of oxygen

Exercises

6. How could you reduce Fe_2O_3 in which iron has a valence number of three? Give an electronic explanation.
7. When magnesium unites with chlorine, how are the electrons lost and gained?
8. In refreshing your memory as to the valence number of an element, what is the advantage of looking up the correct formula of the chloride (index)?
9. Define positive valence number; negative valence number; electrovalence; covalence; coördinate-covalence.
10. If 26 g. of chromium displace 1 g. of hydrogen from hydrochloric acid, what is the valence number of chromium in this displacement?
11. Assuming that chlorine is monovalent and that oxygen is divalent, state the valence number of each of the metals in the following compounds: MgO , AgCl , AlCl_3 , FeO , Fe_2O_3 , SnO_2 , Cr_2O_3 , NiCl_2 , AuCl_3 .
12. Cobaltous oxide is CoO ; cobaltic oxide is Co_2O_3 . Write formulas for two types of cobalt compounds containing any of the following groups: Cl , NO_3 , PO_4 , SO_4 .
13. Molecules of covalent compounds have relatively little attraction for each other and so are readily separated from each other in both their solid state (low melting points) and their liquid state (low boiling points). On the other hand the attraction between ions in ionic crystals is so strong that the melting points of salts are high. So are their boiling points.

Select covalent and electrovalent compounds from those with the following boiling points: HCl , -85° , LiCl , 1337° , NaCl , 1442° , BeCl_2 , 500° , BCl_3 , 12.6° , and CCl_4 , 77° .

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Chapter II WATER AND HYDROGEN PEROXIDE

WATER

History. Cavendish, not content with his pioneering study of the properties of hydrogen, added to his laurels by synthesizing water by igniting a mixture of two volumes of hydrogen and one of oxygen with electric sparks. Lavoisier decomposed water with red-hot iron and clearly interpreted Cavendish's experiments. In 1800 Nicholson and Carlisle decomposed water into its elements by electrolysis, securing two volumes of hydrogen to one of oxygen. This was the first time the electric current was used to bring about a chemical change.

Occurrence. Water is the most essential and most abundant compound. It makes up over two-thirds of the human body. Plant tissue contains from 50 to 75 per cent water. Evidently moisture in the soil and in the air is necessary to plant life.

One inch of rain on the United States corn belt at the critical time in the growing season is worth \$800,000,000. This inch on a single acre weighs 113 tons.

Physical Properties. Pure water is colorless in thin layers, but in thick layers is blue. However, we do not find absolutely pure water in nature. The pleasant taste of good drinking water is due to dissolved air and carbon dioxide. This explains why boiled water is so unpalatable.

One milliliter of water at 4° C. weighs one gram, so by definition its *density* is one gram per ml., a standard for comparison of all solids and liquids. Water expands on being warmed above or cooled below this point, so that its density is greatest at 4° C.

Specific gravity is a mere number representing the ratio of the density of any material to that of a standard, usually water. Since 1 ml. of gold weighs 19.32 g. its sp. gr. is 19.32.

Under 760 mm. pressure liquid water becomes solid ice at 0°C . and gaseous steam at 100°C . In melting one gram of ice at 0°C . into water at 0°C ., 79.7 calories of heat must be absorbed. Conversely, on freezing, one gram of water releases 79.7 calories. This is called the *heat of fusion of ice*.

One gram of water at 100°C . requires 539 calories of heat to change into steam at 100°C . On condensing this steam into water, 539 calories — the *heat of vaporization* — are released.

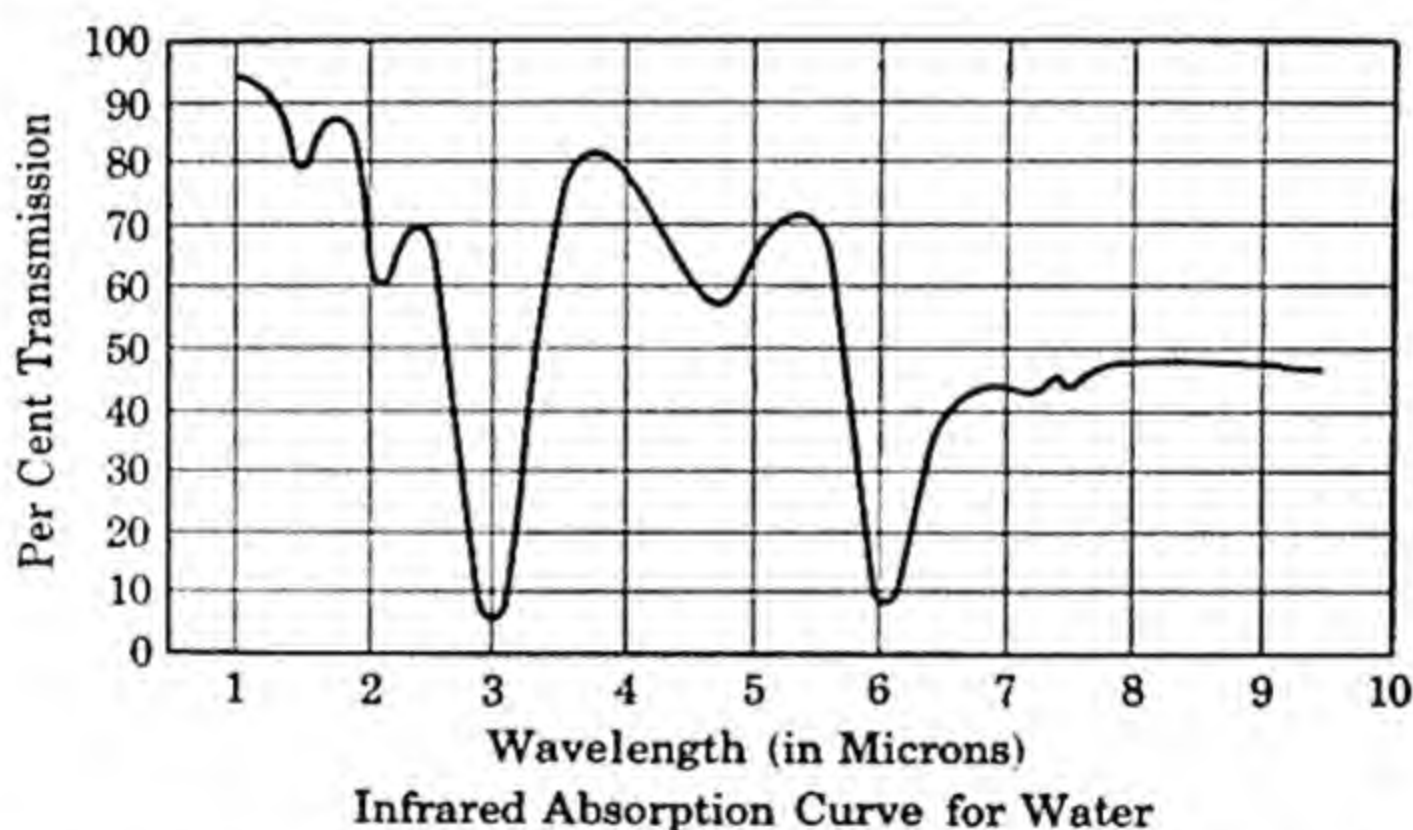
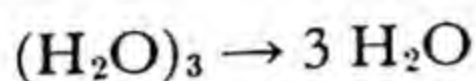


Fig. 55. Every substance, even pure water, records its own finger print on light by absorbing (stopping) certain wave-lengths. See Chapter on Radiation Chemistry. One micron = 10^{-4} cm.

The *specific heat* of water is 1, which means that one calorie of heat is required to raise the temperature of one gram of water one degree. This is greater than the specific heat of almost every other substance. It is for this we prize a hot-water bottle — at times — and enjoy a hot-water heating system. Since the specific heat of many common rocks is only one-fifth that of water, it is evident that great bodies of water heat up slowly and cool off slowly in comparison with land, thus moderating the climatic changes.

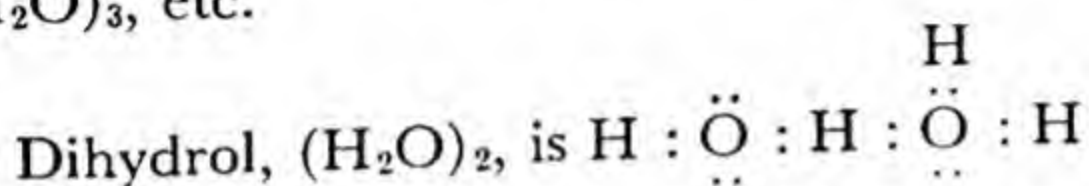
But for the high specific heat of water and the high percentage of water in the human body even gentle exercise would raise our body temperature dangerously, perhaps fatally.

It is possible that the high specific heat of water is the heat of dissociation of trihydrol:



Liquid water is a mixture of H₂O, (H₂O)₂, and (H₂O)₃ in proportions varying with temperature, for ice is largely trihydrol and steam largely monohydrol. Duclaux insists that if water molecules were not associated in this way the liquid would boil at 100° *below* zero. What a readjustment for the world would be necessary in such a circumstance!

The hydrogen bond determines the magnitude and nature of the mutual interaction of water molecules, accounting for (H₂O)₂, (H₂O)₃, etc.



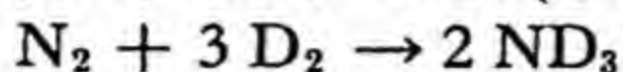
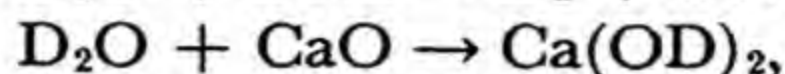
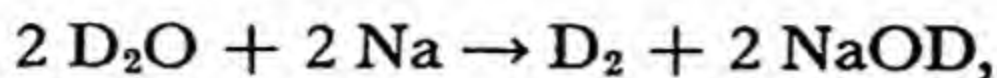
Steam may be superheated so that metal containers become red hot. In the latest steam turbine (a giant with a shaft 75 ft. long) steam at 545° C. and 1250 lb. pressure is sent against the rotating blades. In one-tenth of a second the pressure drops to a fair vacuum (on condensation) and the temperature to about 24° C. Parts of the blades rotate at 1300 feet per second. The shaft is connected with an electric generator of 100,000 kilowatt capacity.

Heavy Water, D₂O. Common water contains about one part in 6000 of D₂O.

The following table gives some of the physical data obtained with heavy water, compared with those of ordinary water:

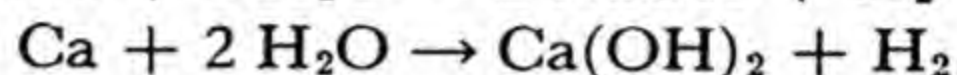
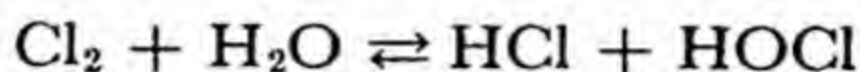
	ORDINARY WATER	HEAVY WATER (99% H ₂ O)
Boiling point.....	100° C.	101.42° C.
Freezing point.....	0.0° C.	3.82° C.
Density (20° C.).....	0.9982	1.1079
Viscosity (20° C.).....	10.87	13.7 (92%)
Refractive index (20° C.).....	1.33293	1.3281
Surface tension (20° C.)	72.75	68.1 (92%)
Solubility of		
NaCl.....	35.9 gms./100 ml.	30.5 g./100 ml.
BaCl ₂	35.7 gms./100 ml.	28.9 g./100 ml.

Some typical reactions:



The resulting compounds differ a little, but not much, from the similar hydrogen compounds in properties.

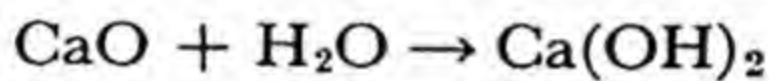
Chemical Properties. Water reacts with some elements, such as chlorine and sodium:



With ammonia it forms the soluble base, ammonium hydroxide:



while with calcium oxide it forms the base, calcium hydroxide:



Exercise

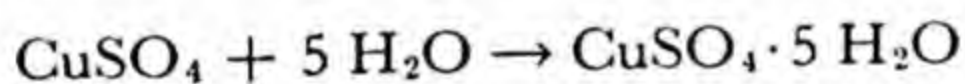
1. What metals react with cold water? What metals react with steam only when very hot? Can carbon be made to react with water? What oxides react with water? See chapter on Oxygen and on Hydrogen.

Calcium carbide reacts with water to yield acetylene, a gas readily recognized by its odor, thus making possible a delicate test for water.

Smith and Bryant, *J. Am. Chem. Soc.*, 57, 841 (1935), detect as little as 0.0002 per cent of water in gasoline by their reagent.

Hydrates. Many crystals are anhydrous. Certain substances crystallize from their water solutions on slow evaporation of the liquid, and carry definite amounts of water with them. This *water of crystallization*, as it is sometimes called, is not held in a wet-sponge fashion, for no amount of pressure will squeeze it out. Moreover a sponge can hold any amount of water, within wide limits. Not so these *hydrates* which we are discussing. Hydrates must be definite chemical compounds because atomic weights are

essential in expressing their composition. The water molecules must be attached to the metal ion by coordinate covalence. Some substances, it is true, can crystallize with two or three definite amounts of water, but the shapes of the crystals, solubility, and some other properties are then different. These hydrates feel dry to the touch but easily lose their combined water when heated. On adding the heated product to water the same solution is obtained as if the crystals had been used. For example, blue vitriol is a hydrate with five molecules of water of crystallization, $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$. When heated above 200° , all the water is lost and a white powder is obtained, CuSO_4 . Under favorable conditions this can be obtained in crystals of a different shape from those of $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$. But add either $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ or CuSO_4 to water and the same blue solution results. On careful evaporation of the two solutions, both produce blue crystals of $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$:

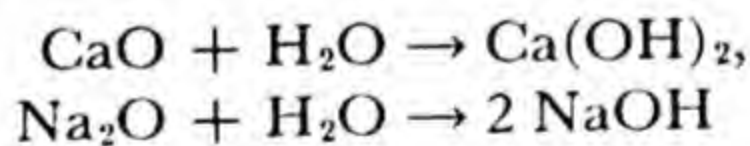


Copper sulfate forms at least three hydrates, $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$, $\text{CuSO}_4 \cdot 3 \text{H}_2\text{O}$, and $\text{CuSO}_4 \cdot \text{H}_2\text{O}$.

Dehydrated copper sulfate gives off 18,500 calories of heat when a gram-molecular weight, or mole, of it unites again with as much water as it held in its original form of $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$.

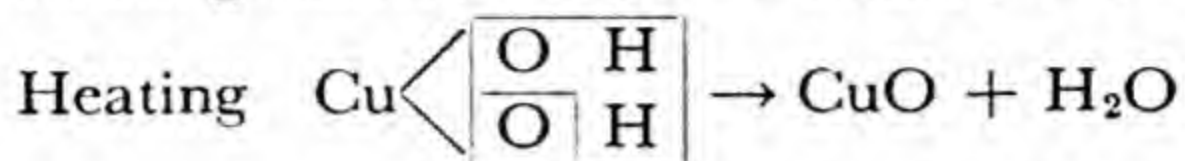
Many minerals, gypsum for example, are hydrates.

Such hydroxides as we have known so far (NaOH , $\text{Ca}(\text{OH})_2$, and KOH) can also be formed by the union of water with the proper metallic oxide.



Hydrates, however, are well-crystallized compounds formed by the union of water with compounds, such as CuSO_4 , or even with an element, such as chlorine. Some hydroxides, like hydrates, lose water readily on heating. Silver hydroxide loses water as fast as it is formed at ordinary temperatures, so that we secure only silver oxide. In fact the oxide may be drowned with water, but it refuses to hold any of it. In hydrates the water molecules retain their identity in the crystal lattice (as shown by X-ray

photographs of their crystals), while in hydroxides the water lost on heating comes from the $-\text{OH}$ groups.



Place a clean crystal of $\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$ in the open air and it soon crumbles to a white powder weighing far less than the crystal. Evidently the outward pressure of the water evaporating from the crystal is greater than the opposing pressure of water vapor in the air. Water is lost until the rates of evaporation and deposition of water molecules become equal.

Such loss of water from hydrates at room temperatures is called *efflorescence*. Washing soda, $\text{Na}_2\text{CO}_3 \cdot 10 \text{H}_2\text{O}$, acts in a similar manner. Other hydrates lose little or none of their water in ordinary air — blue vitriol, for example. This means that the aqueous tension of $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ cannot more than slightly exceed the partial pressure of water vapor in ordinary air. It might be less. But in absolutely dry air blue vitriol loses water.

Deliquescence, the taking up of water vapor by certain very soluble solids, is discussed later.

Drying. It is often desirable to remove moisture from air or other gases. This may be accomplished by the drying agents mentioned below which function as indicated:

By chemical reactions	<div> <div>To form hydrates</div> <div> CuSO_4 $\text{Mg}(\text{ClO}_4)_2$ $\text{Ba}(\text{ClO}_4)_2$ CaSO_4 H_2SO_4 </div> </div> <div> <div>To form acids or bases</div> <div> P_2O_5 CaO BaO </div> </div>
By formation of solutions of low aqueous vapor tension	<div> KOH NaOH CaCl_2 H_2SO_4, in part SiO_2 ("Silica Gel") Al_2O_3 ("activated alumina") </div>
By condensation of water vapor in capillaries	<div> $\text{Mg}(\text{ClO}_4)_2$ $\text{Ba}(\text{ClO}_4)_2$ CaSO_4, in part </div> <div>in part</div>

Ordnance and certain other metal parts crossing the sea during the early part of World War II were exposed to salt air corrosion, unless greased. Later shipments were sealed in waterproof bags containing active silica gel. This ultraporous solid kept the enclosed air very dry.

Natural Waters. The average annual rainfall of the United States is 27.6 inches (falling an average distance of 7920 feet). It would require a three-horse-power engine working a year on



Fig. 56. When Witigis, king of the Goths, brought his hordes to the siege of Rome in 537, he dealt a deadly blow at the city by striking at the aqueducts which furnished Rome with water.

every acre to raise this quantity of water to such a height. Yet the sun's heat through evaporation and air currents accomplishes this great task. Water is the most nearly universal solvent we have. Most substances are dissolved by it to at least a minute extent.

Abundant, pure, cheap water makes the modern city possible. In Colonial days water was peddled around Philadelphia at \$1.00 per 100 gallons while today in large cities 100 gallons of safer water may be had at no inconvenience whatever for one cent.

Our urban population uses over 100 gallons daily per capita and may bring it in gigantic pipes or conduits 100 miles from the mountains (New York) or even 250 miles (Los Angeles).

Purification of Water. Dangerous bacteria in drinking water may be killed by small amounts of chlorine or of chlorine dioxide. If the excess above the amount used up in reaction exceeds one part per million by weight, this excess is sometimes reduced by activated charcoal.

A very common method of treatment is to follow the settling of mud, or of precipitates deliberately produced, by sand filtration.

The typhoid death rate in Detroit in 1911 was 24.5 per 100,000 but one year after chlorination of the water supply was introduced it dropped to 10.9, and later to 4 per 100,000. After filtration, and introduction of chlorine control tests every four hours to guarantee 0.1 part per million by weight of excess chlorine, the typhoid death rate fell to 0.2 per 100,000 (1937) — a scientific triumph. The United States Army requires 0.4 ppm. of excess chlorine.

Nature's methods of purifying river water are interesting. The dissolved organic material is decomposed by bacteria. Sewage is used up, to a great extent, by snails, beetles, mussels, worms, insect larvae, and other organisms. Oxygen and sunlight assist.

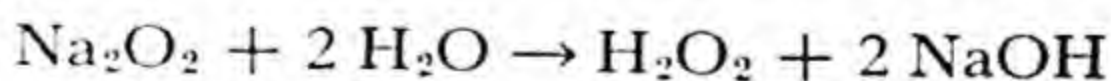
Military purification of water supplies was a vital matter during World War II. Chlorination was common, and individual soldiers were given chloramine tablets to use on emergency supplies. Desalting devices for fliers to use if wrecked on the ocean saved many lives.

Bad taste in city water caused by certain plant growth is combatted by the use of copper sulfate, two to ten pounds per million gallons. This prevents growth of the plants. Activated ultraporous carbon removes taste and odor and chlorine dioxide is said to remove taste and odor due to phenolic wastes.

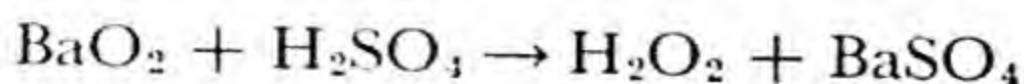
HYDROGEN PEROXIDE

Hydrogen peroxide resembles ozone in its "safe and sane" oxidizing action on delicate materials such as silk and hair. The "100 volumes" solution releases 100 ml. of oxygen at 20° C. and 760 mm. from 1 ml.

Preparation. A convenient laboratory method of preparation is to drop sodium peroxide slowly into ice water:



If too much sodium peroxide is added too rapidly, the heat of reaction decomposes the desired hydrogen peroxide into water and oxygen.



The reaction above is favored commercially for the preparation of the medical grade of H_2O_2 . The barium sulfate, being insoluble, is filtered off from the solution.

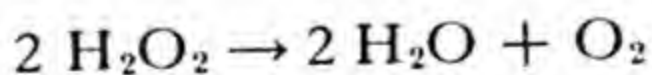
In recent years the commercial practice has changed. Only the pharmaceutical grade is made from barium peroxide. All other grades (much the larger part of the total) are prepared by electrolysis of water solutions of ammonium sulfate, or better, of concentrated sulfuric acid. The persulfuric acid formed at the anode is decomposed by steam, yielding hydrogen peroxide and sulfuric acid:



The most favored concentration for industrial use was 27.6 per cent while the household brand is only 3 per cent by weight. Now 90 per cent concentration is available for industry.

During World War II the Germans produced enormous quantities of 85 per cent hydrogen peroxide, a difficult achievement. Because of its ready release of great volumes of oxygen and its powerful oxidizing property it was used with calcium permanganate, or alcohol, or Diesel oil or hydrazine (N_2H_4) for propulsion of rockets, naval torpedoes, jet propulsion planes and unmanned tanks. Now that an American firm has developed a 90 per cent product (stable for several months) industry will benefit greatly from this war product. As a powerful oxidizing and bleaching agent leaving no residue it has great promise.

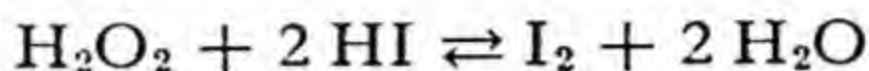
Properties. Hydrogen peroxide, a colorless liquid, mixes with water in all proportions and is comparatively stable in such solutions. Light decomposes it, so brown bottles are the best containers. The trace of alkali from the glass decomposes it, but a very little acid can counteract this tendency by reacting with the alkali. Usually a trace of acetanilide is used to check decomposition:



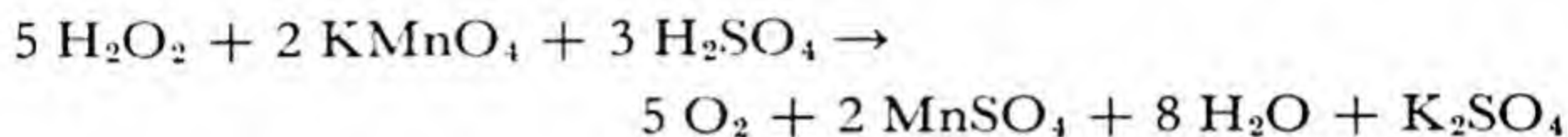
The purer the solution the greater its stability on distillation in the process of concentrating it for industry.

Tests. Like ozone, hydrogen peroxide releases free iodine from hydrogen iodide. In the presence of starch this iodine develops a

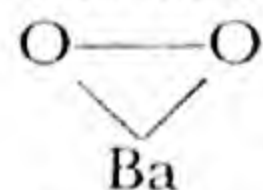
blue color. A filter paper dipped in a solution of potassium iodide and starch paste (slightly acidified to release hydriodic acid) serves as a rough test, but because the oxygen of the air also releases free iodine (though slowly) from hydrogen iodide, the test is good only if a blue color forms almost instantly:



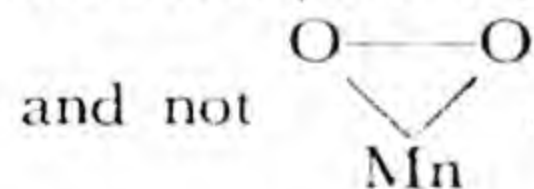
Solutions of hydrogen peroxide decolorize acid solutions of potassium permanganate, thus giving an analytical basis for the determination of concentration of the peroxide solution:



Peroxides. The structural formula of water is $\text{H}-\text{O}-\text{H}$ and of hydrogen peroxide $\text{H}-\text{O}-\text{O}-\text{H}$. Evidently sodium peroxide, Na_2O_2 , is a salt derived from the feeble acid H_2O_2 by replacement of the hydrogen with sodium. (This is not done directly, however.) $\text{Na}-\text{O}-\text{O}-\text{Na}$ is the structural formula for this oxide. When BaO_2 is acidified, $\text{H}-\text{O}-\text{O}-\text{H}$ is formed, so



must represent the structure. But MnO_2 when acidified does not yield H_2O_2 . Hence its structure must be $\text{O}=\text{Mn}=\text{O}$



and not Mn . Peroxides yield hydrogen peroxide when acidified and dioxides do not. MnO_2 and PbO_2 should be called dioxides. In the true peroxide linking, two oxygen atoms are directly attached to each other.

Zinc peroxide is used in cosmetics (bleaching creams) and in medicine as a deodorant on certain types of ulcers.

Per-Salts. Certain salts such as the sodium or potassium carbonates and borates are crystallized from cold solutions of hydrogen peroxide to yield perborates, percarbonates, etc. Zinc perborate has value as an antiseptic dusting powder. Often perborates are used as bleaching agents, since these yield hydrogen peroxide in the presence of water and are therefore very suitable.

Washing powders may contain perborates, sodium carbonate, sodium silicate, and powdered soap.

Above 40° a water solution of sodium perborate evolves oxygen gas, probably resulting from decomposition of the hydrogen peroxide first formed.

Exercises

2. How was deuterium discovered? Isolated?
3. If a crystal of a given hydrate does not lose water in the open air at 20° , how could you force it to effloresce?
4. Would all hydrates effloresce in a vacuum?
5. Lead dioxide, PbO_2 , does not yield H_2O_2 when treated with an acid (H_2SO_4 , for example). What, therefore, must be the structural formula of this oxide of tetravalent lead?
6. What is meant by the heat of fusion of ice? By the heat of vaporization of water?
7. How much chlorine per million gallons is used in water purification?
8. Glauber's salt is a hydrate of sodium sulfate. If 12 g. of Glauber's salt, when heated, lose 6.72 g. of water, what is the formula of the hydrate?
9. If 90 ml. of hydrogen and 58 ml. of oxygen are exploded in a closed tube, which gas remains? How much?
10. Diethylene glycol is used to dry natural gas before treatment with refrigeration and compression to obtain high-test gasoline. Why the preliminary drying?
11. How is a gas dried by solid KOH ? By solid anhydrous CaCl_2 ? By concentrated H_2SO_4 ? By ultraporous Al_2O_3 or SiO_2 ? By anhydrous CuSO_4 ?
12. One milliliter of lead weighs 11.34 grams, therefore its specific gravity is 11.34. As an extreme instance one cubic inch of the companion star to Sirius weighs three tons. Its density? Its specific gravity?

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Chapter 12 CARBON AND ITS OXIDES

CARBON

Nearly 500,000 compounds of carbon are known (though not by any one man). All other compounds of the other elements make up only a small fraction of this impressive number, perhaps 25,000. Carbon chemistry was named Organic Chemistry because it was once thought that only organized living matter could produce carbon compounds. In other words, only plants and animals qualified as synthetic carbon chemists. But since 1828 a very great number of these compounds have been made in the laboratory.

The importance of carbon and its compounds is evident as we learn that they make up our fuels (whether coal, wood, oil, or gas); our lubricants; our foods; our clothing; and that they make possible the change from iron to steel. Drugs, dyes, explosives, auto finishes, pencils, picture film, printer's ink — these and a host of other necessities are based upon carbon and its compounds.

Carbon is tetravalent as shown by the compounds CH_4 , CCl_4 , and CO_2 , and it is a non-metal as indicated by the acid (H_2CO_3) formed when its oxide (CO_2) is dissolved in water. It resembles silicon, tin, and lead (of the same group in the Periodic System) in some respects, although it is not metallic like tin and lead.

The element occurs in nature in two crystalline forms: the diamond and graphite. It is readily prepared from its compounds in such amorphous forms as coke, lampblack, charcoal, bone-black, and carbon black.

The Diamond. The diamond, a pure form of carbon crystallizing in the regular system, has a density, 3.5 g. per ml., which is greater than that of graphite and the other forms. It is the hardest substance known and hence scratches all other substances. Faulty specimens are used for the cutting edge of rock drills or to make cutting wheels for the machine shop. Brazil and South Africa are our chief sources of industrial diamonds. Their value to industry is great.

The largest diamond ever found, the Cullinan, weighed 3024 carats before it was cut into several smaller but better gems. Since the carat (metric) now equals exactly 0.2 g., this means a crystal of 605 g., or 1.37 pounds. The magnificent Regent diamond, for years seen at the Louvre, weighs 136 carats.

Cost gives the diamond much of its charm, but it has a real beauty when skillfully cut. This is due largely to its high index of refraction. Rays of light are reflected from the interior surfaces of the facets several times before emerging, hence the flashing play of light.

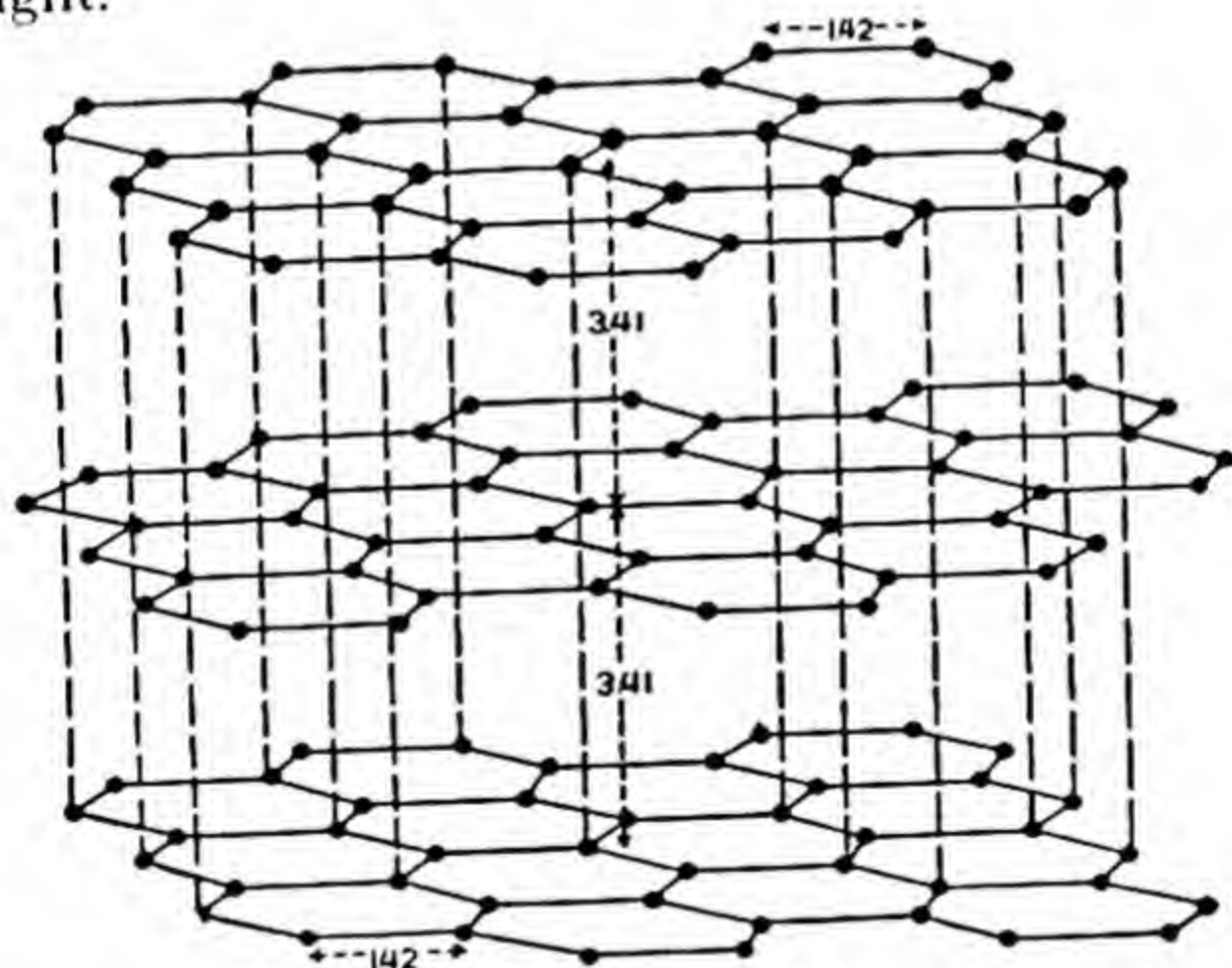


Fig. 57. The crystal lattice of graphite.

Graphite. Graphite is a crystalline form of carbon differing noticeably from diamond. It is black, soft, and lighter than the diamond, having a density of only 2.26. Chemically it is quite inactive, yet it is possible to burn it at very high temperatures.

In graphite there is a hexagonal array of carbon atoms in flat planes, but between planes the distance is two or three times that between atoms in the hexagonal ring. When your lead pencil leaves a mark on paper, the pressure exerted forces slippage of one plane along its neighbors.

When any form of carbon is heated in the electric furnace, it turns into graphite; in fact carbon volatilizes at 3810° K. and on cooling condenses as graphite. This is the basis of Acheson's method of making artificial graphite at Niagara Falls. We import much natural graphite from Ceylon, Madagascar, and Mexico for use in dry batteries, foundry facings, pencils, etc.

The development of carbon and graphite electrodes has made possible the modern electric furnace and electrolytic cell.

Amorphous Carbon. There are several forms of impure amorphous carbon, such as coke, charcoal, and soot, but none of these occur in nature.

Coke. When bituminous coal is heated in retorts without access to air, many useful, volatile products escape and are recovered. These include ammonia, illuminating gas, and coal tar, from the last of which benzene, toluene, phenol (carbolic acid), creosote, naphthalene, and many derivatives of great value are secured. Coke is left behind in the retort. It is used to the extent of 60,000,000 tons yearly in making pig iron from iron ore, in melting metals for foundries, as a domestic fuel, and in the manufacture of some carbon compounds.

Coke burns with almost no flame and no smoke. It is impure carbon since the mineral content of the coal is still in the coke.

Coal. The forests of previous ages were buried under deep layers of earth and so subjected to great heat and pressure. This caused a loss of much volatile material and left coal. Lignite, or brown coal, represents an early stage in nature's coal making, and contains 30-50 per cent water; hence lignite has only moderate fuel value. Enormous deposits are found in North Dakota and other Western states. Bituminous or "soft" coal represents a more advanced stage of coal making in the earth. It yields much combustible volatile matter when distilled and burns with a smoky flame. Anthracite or "hard" coal is almost the final product in coal making. Since nearly all volatile matter has been driven off

in the depths of the earth, the anthracite is hard, yields but little volatile matter on destructive distillation, and burns with no smoke and but little flame. The greatest anthracite deposit in the world is found in eastern Pennsylvania.

The United States is particularly fortunate in its wealth of coal. The world produces about 1,200,000,000 tons annually, and of this over one-half is mined in this country.

Recent research makes possible a smokeless fuel by heating soft coal in a retort for only three minutes at 500°. While still hot enough to be plastic the product is extruded in rods. The by-product gases of coking may be recovered.

Charcoal. Wood charcoal was once used in metallurgy in place of the coke of modern times and it is still in some demand for razor-steel manufacture. Cheap black gunpowder requires it. Just as coke is the non-volatile product of coal distillation, so is charcoal the residue remaining when wood is destructively distilled. By modern methods all the volatile products are condensed and used in many important industries. Among these products are wood alcohol, acetone, and acetic acid.

Carbon Black. When a smoky natural gas flame is chilled, the incandescent carbon of the yellow flame deposits as a form of soot called *carbon black*. Only 5 per cent of the carbon in natural gas is recovered as ordinary carbon black, but the yield of the newer "furnace black" (which can be used in synthetic rubber) is 25 per cent. An inferior carbon called *lampblack* is prepared by chilling the smoky flame from tars and oils.

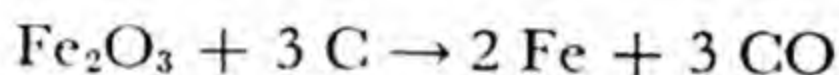
Carbon black is essential to the manufacture of printer's ink and some rubber goods. This black was first used as a filler and strengthener of auto tires about 1912 and then only because of a shortage of zinc oxide. Carbon black doubles the tensile strength of rubber tires and quadruples the abrasion resistance. In a set of tires for a small car there are 12.5 pounds of carbon black and four or five times as much in the larger tires.

Acetylene black, a recent commercial product, made by the heat splitting of acetylene, C_2H_2 , makes rubber electrically conducting, a desirable property for tires, rubber belts, etc. It is by far the best carbon for dry cells.

One ton of natural rubber (exclusive of filler and fabric) requires 460 pounds of carbon black, if tires are to be made. One ton of the most common synthetic rubber requires 950 pounds of carbon black.

Carbon blacks are also used in the manufacture of paints, stove polish, phonograph records, carbon paper, crayons, black leather and other articles, but rubber uses 95 per cent of the total supply of such carbons. Over 400,000,000,000 cubic feet of natural gas are burned annually in the United States to make about 1,000,000,000 pounds of carbon black. Common black smoke is not pure carbon by any means. Nor is it an asset to a city. A year's soot fall on a square mile of London weighs 260 tons.

Chemical Properties. Carbon is inactive except when hot. At higher temperatures it unites readily with oxygen to form carbon monoxide and carbon dioxide. It is our most important commercial reducing agent because when hot it removes oxygen from metallic oxides. This is one of the minor reactions taking place in the blast furnace:



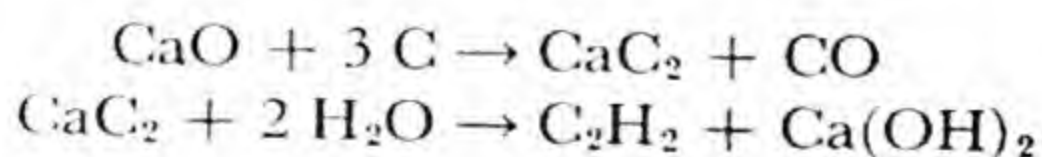
With relatively little coke and excess air the dioxide is formed, but with an excess of coke the carbon monoxide predominates.

Carbon unites with hydrogen to a very limited extent in the electric arc to form acetylene, C_2H_2 , and, by the catalytic aid of nickel powder at 250°C ., to form methane, CH_4 .

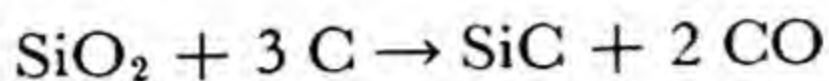
Exercise

1. How could you prepare carbon from methane?

The Carbides. A carbide is a simple compound of carbon with one other element. A carbide of iron, Fe_3C , is found in steel and has great influence on the properties of the steel. *Calcium carbide*, CaC_2 , is the product of electric-furnace heating of lime and coke (cheap raw materials), and reacts with water to form acetylene, C_2H_2 .



A carbide of silicon, sold by one firm as *carborundum*, SiC , one of the most useful abrasives known, is likewise prepared in an electric furnace but from a mixture of coke and sand:



Tungsten carbide ("carboly") and *tantalum carbide* are also used because of their extreme hardness. *Boron carbide*, B_4C , is hard enough for use as the nozzle of sandblast apparatus.

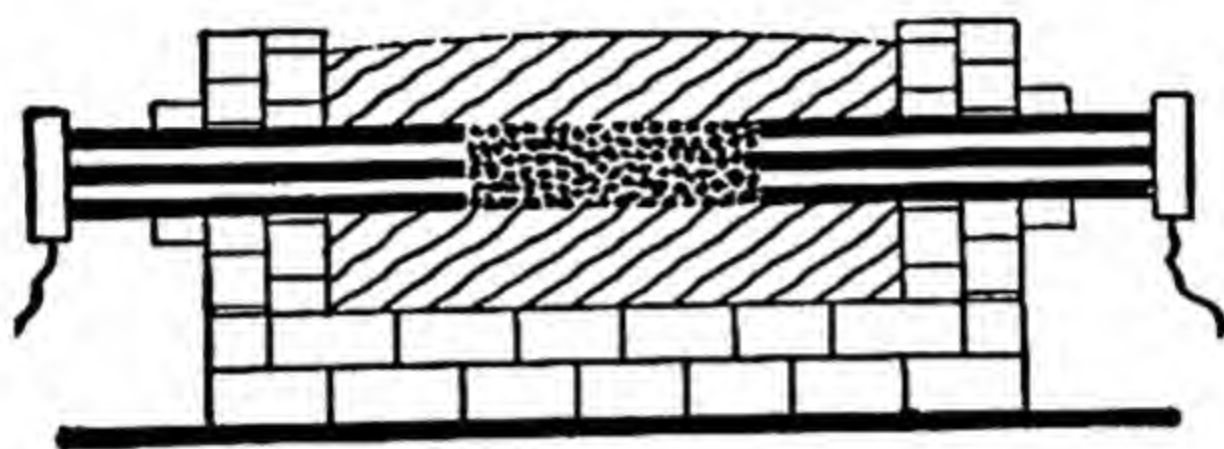
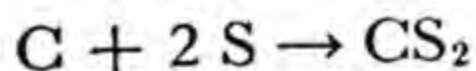


Fig. 58. Silicon-carbide furnace.

Synthetic abrasives to the amount of 8,000,000 tons or more are annually required by the machine shops of this country for grinding, cutting, and polishing.

Carbon disulfide, a heavy, volatile, and highly flammable liquid of valuable solvent properties, is easily made in an electric furnace (with exclusion of air, of course) from charcoal and sulfur:



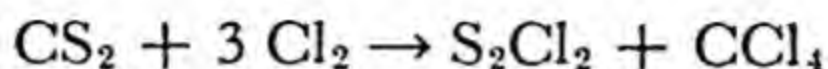
One pound is needed in the manufacture of three pounds of viscose rayon. Our annual production is 165,000,000 pounds.

A new process of preparing carbon disulfide was discovered in 1944. Methane, of natural gas and sulfur vapor react at 700°C . in presence of a catalyst as follows:



Only wood charcoal is suitable for the manufacture of carbon disulfide. Recently it was found that salts of sodium catalyzed the carbonization of wood to make the charcoal 30 per cent more reactive with sulfur. Two other sulfides of carbon are known but they are not important.

Carbon tetrachloride, a colorless liquid and a valuable but non-flammable commercial solvent, is made by passing dry chlorine into carbon disulfide in the presence of a little iodine as catalyst:



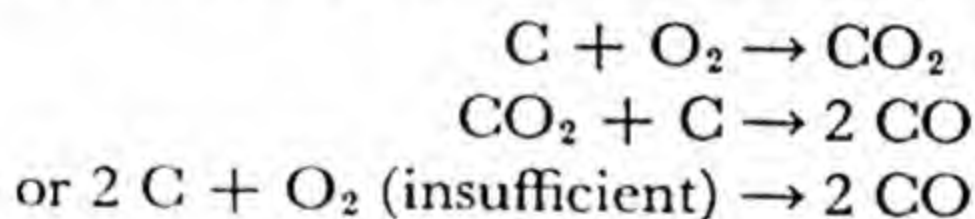
We use 200,000,000 pounds yearly in fire extinguishers and as a grease solvent.

OXIDES OF CARBON

Carbon Dioxide, CO_2 . Carbon dioxide occurs in the air to the extent of 3 or 4 parts in 10,000 and issues from the earth in certain crevices and from some oil wells. One gas well in Utah produced carbon dioxide which was 98 per cent pure.

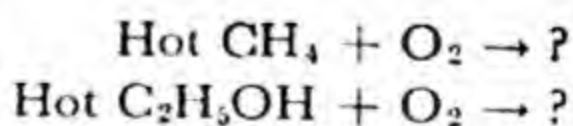
The sea is a tremendous reservoir of carbon dioxide, holding thirty times the amount present in the atmosphere. As much more is locked up in the carbonates of the earth's crust.

Preparation. 1. The simplest method of preparing carbon dioxide is by direct union of carbon and sufficient oxygen. The carbon must be burned with an excess of oxygen or part of the dioxide may be reduced to carbon monoxide by the hot carbon:



But it is not necessary to burn pure carbon. Many carbon compounds, such as coal, wood, paper, and oils, may be burned with formation of the dioxide and other gases.

2. Balance the equations:



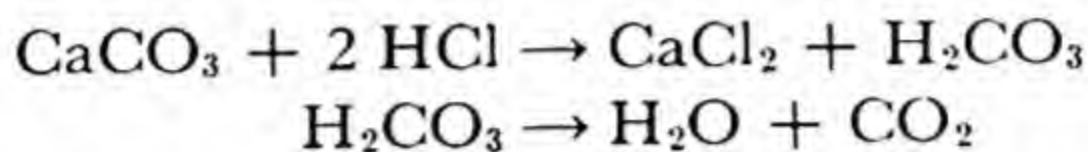
The first represents the burning of natural gas and the second the burning of alcohol.

2. High heating of some carbonates (but not of the carbonates of sodium and potassium) yields carbon dioxide. The manufacture of quicklime from limestone in the limekiln depends upon

this reaction. In a closed tube this reaction is reversible, but it goes to completion if the gas is removed:



3. The usual laboratory method is the treatment of carbonates, such as limestone or marble, with a dilute acid:



The carbonic acid first formed is very unstable, and decomposes with the escape of carbon dioxide.

4. The fermentation of sugar solutions to form alcohol yields carbon dioxide as one product.

Physical Properties. Carbon dioxide is a colorless, odorless gas, one-half heavier than air. At 15° C. water dissolves its own volume of the gas. The soda water of fountains contains much more in solution under about 10 atmospheres pressure. The solution has a slightly sharp, pungent taste. The gas is sold commercially in thick steel cylinders under 60 atmospheres pressure. Most of it is liquid. The liquid, allowed to escape from the inverted cylinder (Fig. 59), vaporizes so rapidly that it is quickly cooled to -79° C., at which temperature one-half of it freezes to a snowlike solid. This may be caught in a cloth bag. Such carbon dioxide snow, "dry ice," is now sold commercially in compressed blocks (to the extent of 700,000 tons yearly).

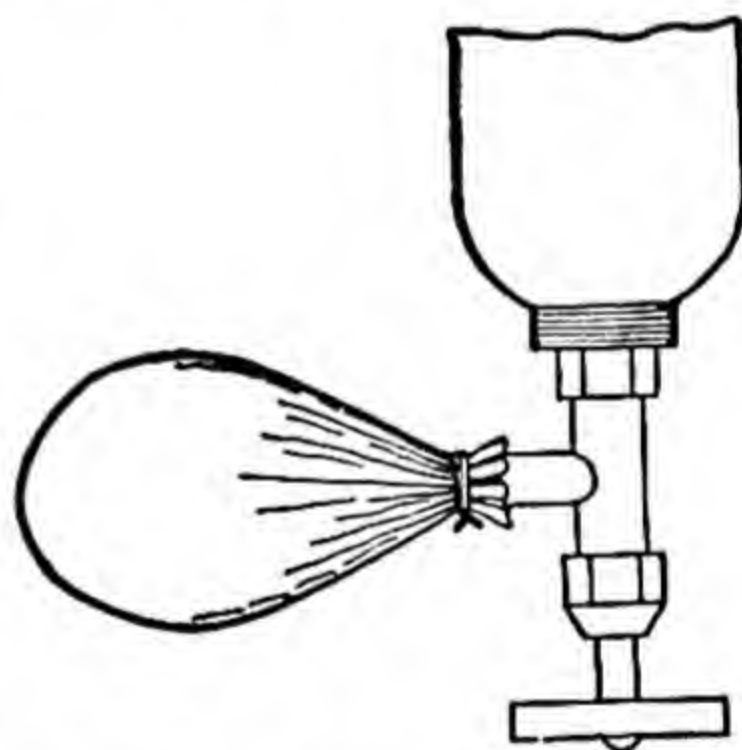


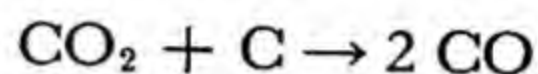
Fig. 59. Making carbon dioxide snow by expansion of the gas through a canvas bag.

Some very spectacular experiments may be performed with this snow. Rapid evaporation of a mixture of carbon dioxide snow and ether makes it a simple matter, by use of this mixture, to freeze mercury (-40° C.). If the mercury is placed in a small pasteboard box and a stick of wood held in it, a hammer is formed with a head of solid mercury. The pasteboard box is

readily torn off and nails may be driven into a board with the hammer. A rubber ball thus chilled breaks to pieces when thrown against a brick wall. A frozen flower is extremely brittle and a frozen rubber tube may be snapped in two like a clay pipestem.

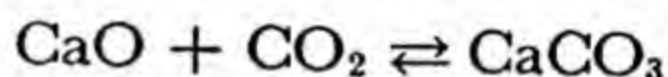
Dry ice has been used to shrink steel castings for fitting to their jackets. Most of it, however, is used in preserving ice cream.

Chemical Properties. Magnesium burns in the dioxide, leaving black carbon. Carbon above 1000° (almost white heat) readily reduces carbon dioxide to the monoxide:

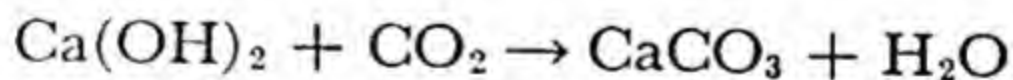


In a furnace with a deep bed of brightly glowing coals the carbon dioxide formed at the bottom of the layer is reduced to the monoxide by the upper layers of incandescent coal. The monoxide then burns at the surface with a blue flame.

With metallic oxides carbon dioxide unites to form carbonates — a reaction readily reversed at high temperatures:



Quicklime exposed to the air not only takes up moisture, becoming “air slaked,” but slowly reverts, as indicated by the equation, to calcium carbonate:



Oxygen used for resuscitation of drowning persons is more effective if mixed with 5 per cent of carbon dioxide, which seems to stimulate the muscles used in breathing.

Carbonic Acid, H_2CO_3 . Since a water solution of carbon dioxide is weakly acid, there must be a reaction between water and

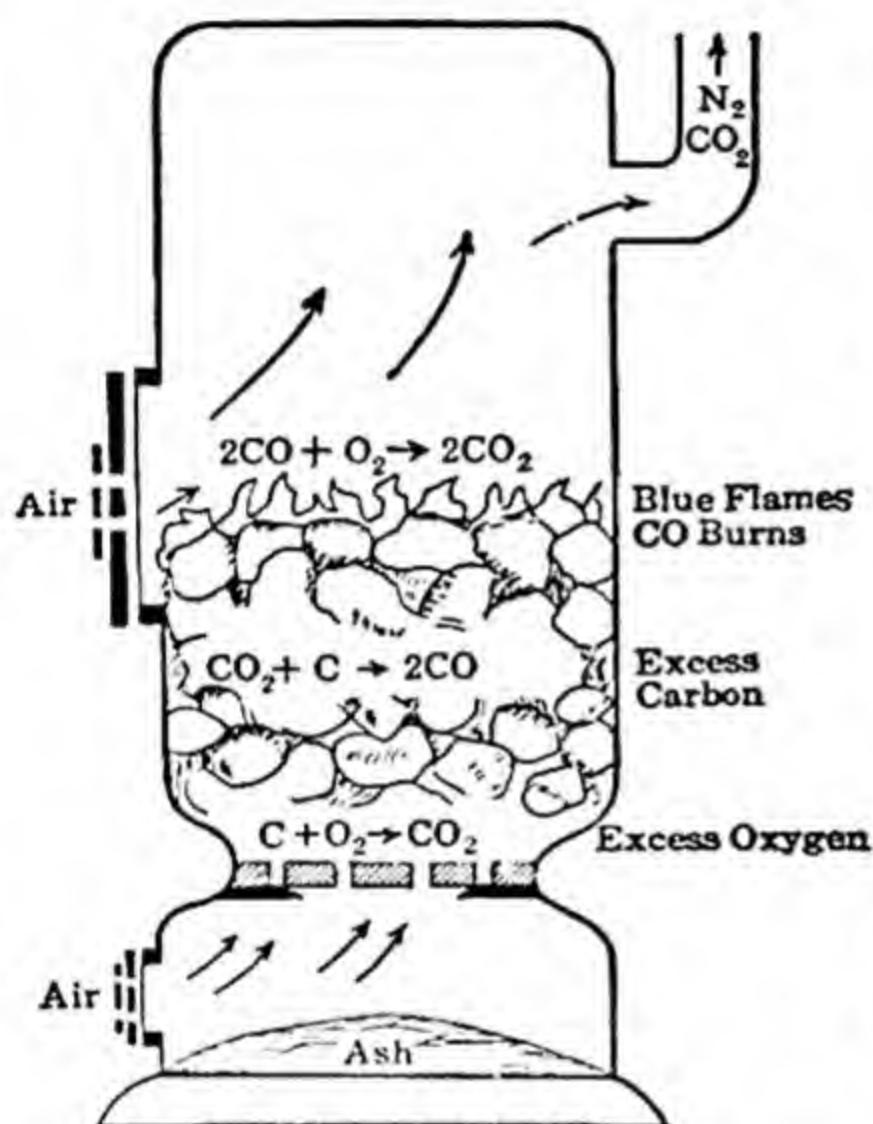
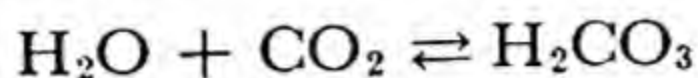


Fig. 60. Chemical reactions in a common furnace.

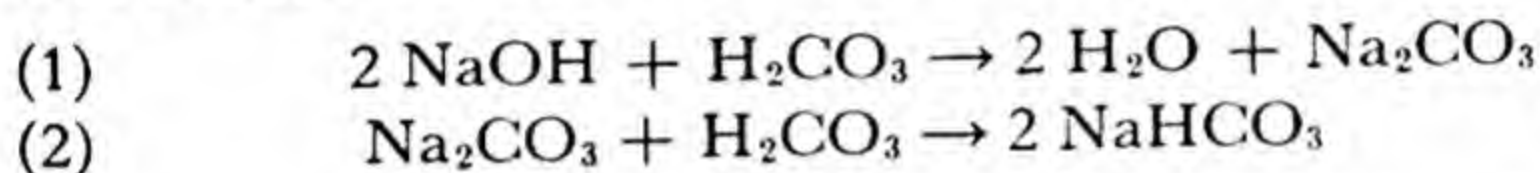
carbon dioxide to form an acid, carbonic acid. On boiling, all the carbon dioxide is removed, so the reaction is evidently reversible:



The water solution has a pleasantly sharp taste, hence its use as plain soda water. One might realize that the acid is weak by reflecting that the moisture and carbon dioxide of the lungs certainly do not injure the tissues of the lungs as would be the case if carbonic acid were a strong acid.

What would happen if you bubbled pure air through a solution of carbon dioxide? Why?

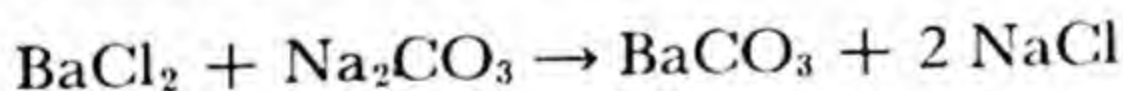
Carbonates and Bicarbonates. Passage of carbon dioxide into a solution of a base yields carbonates or bicarbonates, depending on the relative amounts of carbon dioxide used. The carbonic acid formed simply is neutralized by the base:



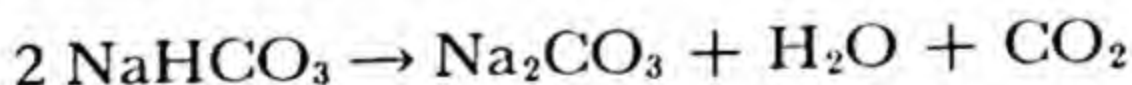
Reaction (1) becomes (2) when an excess of carbon dioxide is bubbled through the solution.

An excess of carbon dioxide in soil waters dissolves limestone by formation of the soluble calcium bicarbonate ($\text{CaCO}_3 + \text{H}_2\text{CO}_3 \rightarrow \text{Ca}(\text{HCO}_3)_2$). The water then becomes "hard."

All carbonates are insoluble except those of the sodium group. Thus an easy way to precipitate the insoluble ones is to add any soluble carbonate to a solution of any salt of the desired metal.



When heated all bicarbonates are decomposed into carbonates, water, and carbon dioxide:



Sodium bicarbonate (NaHCO_3) is common baking soda.

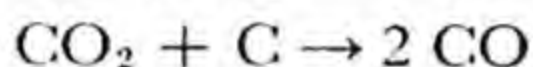
Dimethyl carbonate, $(\text{CH}_3)_2\text{CO}_3$, is a new solvent for plastics and resins.

Uses of Carbon Dioxide. The Solvay process (Chapter 36) of making sodium carbonate and sodium bicarbonate requires

500,000 tons of carbon dioxide annually. Since this industry also uses lime, it is the best economy to burn limestone in a limekiln and thus secure both carbon dioxide and calcium oxide. There is no need to liquefy the gas for this industry.

Carbon dioxide foams are useful in suppressing fires. In one type of extinguisher two solutions are mixed upon inversion of the apparatus. Carbon dioxide formed exerts the pressure needed to expel the contents as a foam consisting of minute, tough bubbles of carbon dioxide which blankets the fire.

Carbon Monoxide, CO. This colorless, poisonous, almost odorless gas is formed by burning carbon with an insufficient supply of air or by passing carbon dioxide over very hot carbon:

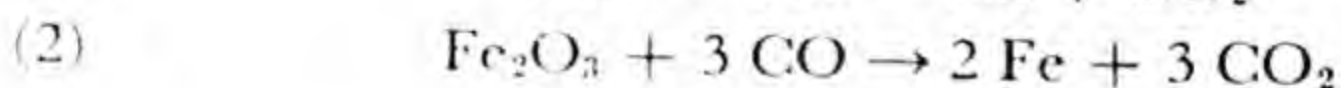
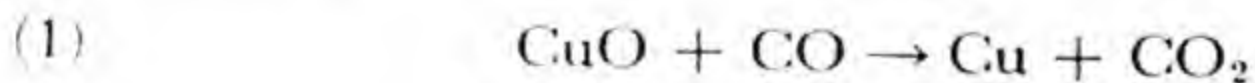


Great care must be used when carbon monoxide is present. Leaky domestic furnaces, and motors warming up in closed garages, offer the greatest hazards, for the gas is odorless as well as poisonous. Auto exhaust contains about 7 per cent.

A concentration of 0.02 per cent may cause headache in a few hours; 0.06 per cent will cause it in less than one hour, and will bring unconsciousness in two hours. Nausea may occur.

The poisonous action of carbon monoxide depends on the fact that it has a much greater affinity for the hemoglobin of the blood than has oxygen — hemoglobin attracts carbon monoxide about 200 times as strongly as it does oxygen.

Carbon monoxide is a good reducing agent, and extracts oxygen from hot metallic oxides:



Carbon monoxide is really an important chemical raw material. From it are made methyl alcohol (methanol), phosgene, cyanides, organic acids, aldehydes, ketones, and metal carbonyls.

Iron carbonyl, $\text{Fe}(\text{CO})_5$, is an excellent antiknock agent in gasoline but the iron oxide deposit may damage the engine. Like tetraethyl lead, the present antiknock agent, it is very poisonous. The formation of volatile nickel carbonyl is important in the metallurgy of nickel ores.

The Cycle of Carbon in Nature. Nearly all the vast amount of carbon dioxide thrown into the atmosphere by processes of

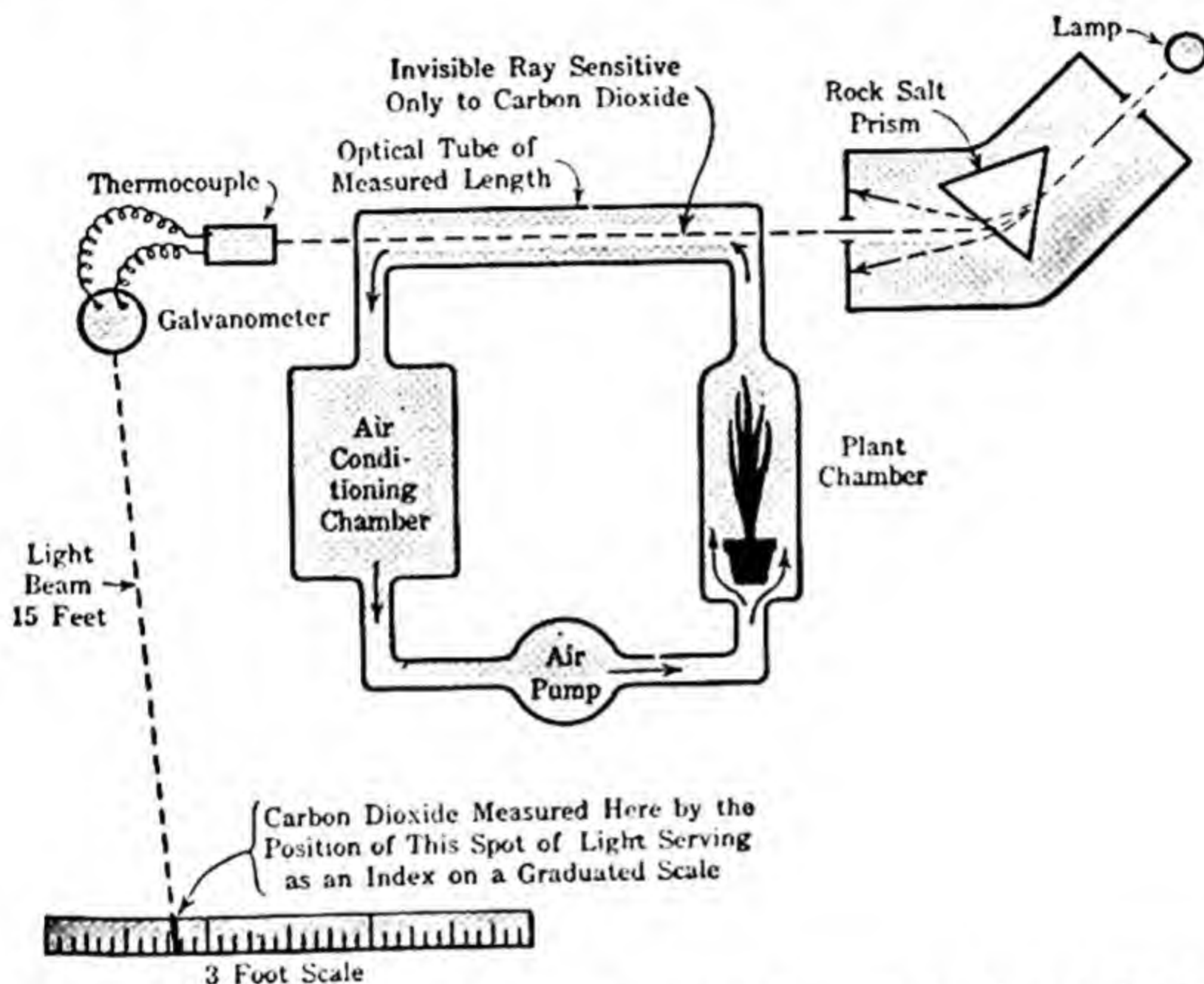
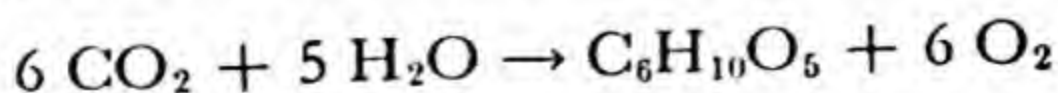


Fig. 61. Carbon dioxide can absorb, or block the passage of, a beam of light of a certain wave length selected as shown here. So sensitive is this apparatus that in 30 seconds the robbing of the atmosphere of carbon dioxide by a 6-inch wheat seedling is indicated by movement of the beam of light reflected from the galvanometer mirror. Change in radiation energy sets up a current in the thermocouple. (Courtesy E. D. McAlister and *Country Gentleman*.)

combustion, of decay, fermentation, and animal respiration is taken up by plants as a valuable food. In the sunlight chlorophyll, the green coloring matter of leaves, is formed and this catalyzes the following endothermic reaction:



The $\text{C}_6\text{H}_{10}\text{O}_5$ represents cellulose of wood, etc.

Exercises

3. What is the difference between silicon carbide and calcium carbide?
4. Distinguish between carbon black and lampblack. Which is the better and why?
5. What volume of oxygen would be required to burn 80 liters of carbon monoxide? What volume of carbon dioxide would be formed?
6. Suppose you wished to prepare 50 liters of CO_2 by the action of hydrochloric acid on marble. What weight of hydrogen chloride and marble would be required?
7. A compound has the following composition: carbon 26.5 per cent, hydrogen 2.2 per cent, oxygen 71.2 per cent. What is the compound?
8. What volume of acetylene at 20° and 740 mm. is obtained by the action of water on 16 g. of calcium carbide?
9. How many grams of carbon dioxide result upon heating adequately seven kilograms of pure marble (calcium carbonate, CaCO_3)?
10. One liter of carbon dioxide at one atmosphere pressure weighs 1.97701 g. Calculate the molecular weight.
11. How many milliliters of carbon dioxide (standard conditions) will be released by heating 400 g. of sodium bicarbonate?
12. Suggest methods of reducing smoke in our cities.

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Chapter 13 MOLECULAR AND ATOMIC WEIGHTS

Dalton, Gay-Lussac, Avogadro. In 1805, just after the publication of Dalton's atomic hypothesis, Gay-Lussac found by laboratory experiment that *in any chemical reaction the volumes of all gases concerned stand to each other in the ratios of small whole numbers.* Avogadro in 1811 sought to explain this and other facts by his famous hypothesis that *equal volumes of all gases, under the same conditions of temperature and pressure, contain the same number of molecules.*

Development of Exact Weights. From the above it is evident that if we weigh equal volumes of gases under like conditions, we get weights that are in the same ratios as the weights of *single molecules.* In other words, we can get the relative molecular weights of all gases. (Solids and liquids must be handled differently.)

After attempts to use an exact weight of "1" for the oxygen molecule it was finally decided to compare all other molecules to a weight of 32 for the oxygen molecule. This (by comparing weights of equal volumes) gave 2.016 as the weight of the hydrogen molecule.

Gay-Lussac, early in the last century, had observed that one volume of hydrogen unites with one volume of chlorine to form two volumes of hydrogen chloride. But by Avogadro's theory the two volumes of hydrogen chloride contain twice as many molecules as the one volume of hydrogen. Now *every* molecule of hydrogen chloride contains *some* hydrogen. There is only one way for a given number of hydrogen molecules to be represented in

twice that number of hydrogen chloride molecules. Each hydrogen molecule splits into two parts and each half-molecule is found in each molecule of hydrogen chloride. In other words there must be two atoms of hydrogen in a molecule of hydrogen.

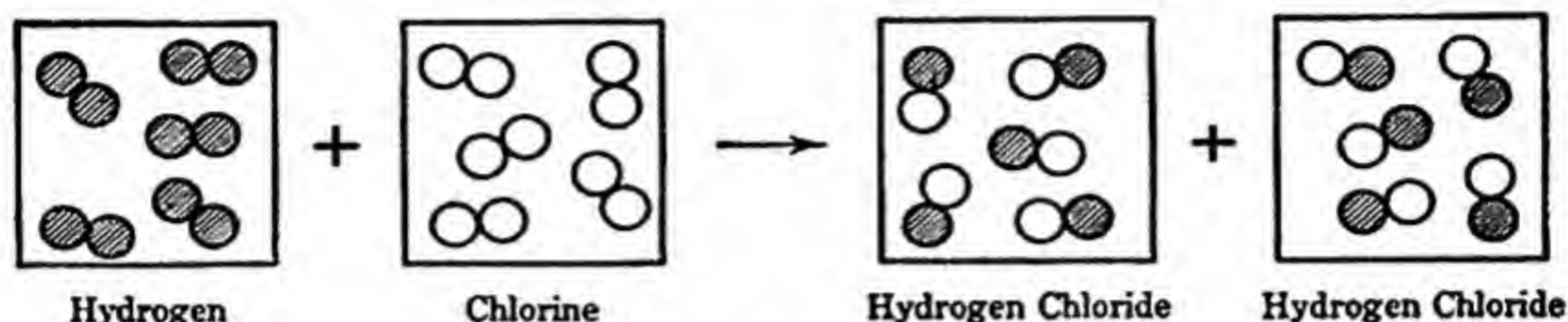


Fig. 62. One volume of hydrogen reacts with one volume of chlorine to form two volumes of hydrogen chloride.

This is probably but not necessarily true from the reasoning above. If the hydrogen molecule were H_4 or H_6 , etc., it could be split into two parts in reaction.

Gay-Lussac also observed that one volume of oxygen unites with two volumes of hydrogen to form two volumes of water vapor. By logic similar to that used above he deduced (as you may also) that there must be two atoms in one molecule of oxygen, the formula of which is then set as O_2 .

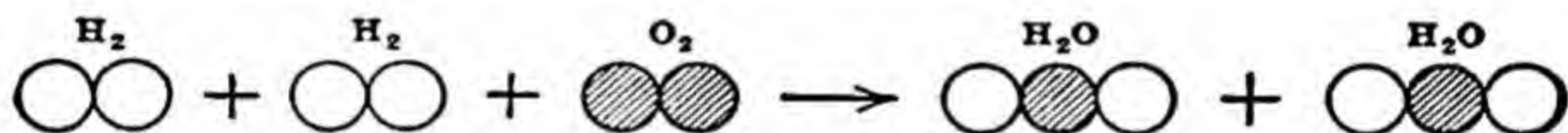


Fig. 63. Two molecules of hydrogen unite with one molecule of oxygen to form two molecules of water.

Cannizzaro's Suggestions. Avogadro's useful theory was not taken seriously until long after his time. Scientists were sadly confused as to the distinction between atomic weights and molecular weights. Then in 1858 Cannizzaro, another Italian, offered a few suggestions that cleared away the confusion. He insisted that molecules of elements were made up of atoms of the same kind and that molecules of compounds were made up of atoms of different kinds. To develop a system of exact atomic weights he suggested that:

1. *The molecular weights of all the volatile compounds of the element studied should be determined.*
2. *These compounds should all be analyzed and the part of each molecular weight due to the particular element determined.*

3. *The smallest weight of the element found in any of the molecular weights of its compounds should be selected as the atomic weight.*

If the complete table of molecular weights of many thousand oxygen compounds were listed in this way, you would note that the smallest part of any molecule due to oxygen is 16. Is it not practically certain that out of thousands of chances nature would put just one atom of oxygen in some molecules? If so, does not the smallest amount of oxygen (16) in any molecule represent the weight of one atom? Therefore should not the *atomic weight* of oxygen be 16? Gay-Lussac arrived at the same conclusion by a rather limited method (already given). By Cannizzaro's logic the atomic weight of chlorine could be deduced from a study of many chlorine compounds. So also for any other element.

LIMITED PORTION OF A TABLE FROM WHICH ATOMIC WEIGHTS COULD BE SELECTED

SUBSTANCE	MOLECULAR WEIGHT	WEIGHTS OF ELEMENTS IN MOLECULAR WEIGHTS OF COMPOUNDS						MOLECULAR FORMULA (?)
		HYDROGEN	CHLORINE	OXYGEN	CARBON	PHOSPHORUS	NITROGEN	
Water	18.016	2.016		16				
Hydrogen chloride	36.468	1.008	35.46					
Methane	16.032	4.032			12			
Acetylene	26.04	2.016			24			
Ethylene	28.05	4.032			24			
Benzene	78.11	6.048			72			
Carbon tetrachloride	153.84		141.84		12			
Carbon dioxide	44.01			32	12			
Phosphorus pentoxide	141.96			80		61.96		
Ammonia	17.03	3.024					14.008	
Phosphorus trichloride	137.35		106.38			30.98		
Alcohol	46.07	6.048		16	24			
Ether	74.12	10.08		16	48			
Nitrogen trioxide	76.02			48			28.016	
Nitric acid	63.02	1.008		48			14.008	

This table allows you to deduce the atomic weights of H, O, C, Cl, P, and N.

Let us deduce the formula of water. Analysis would show that about $\frac{8}{9}$ of any quantity of water taken, or of one drop, or of the smallest particle with all the properties of water (the molecule), is oxygen. This fraction of $18.016 = 16$. Since the weight of one atom of oxygen = 16 (as just shown), there must be only one atom of oxygen in the molecule of water. The part of the molecular weight, 18.016, due to hydrogen is, of course, 2.016 or the weight of two atoms, and the formula must be H_2O . Of course molecular weights are expressed in atomic weight units.

Exercise

1. With the logic used in connection with the selection of the atomic weight of oxygen and the development of H_2O as the correct formula for water, proceed to select from the table above the atomic weights of the six elements used and calculate the formulas of the compounds named in the table.

Hand in a copy of your completed table.

There is not space here for a table of all the compounds of these elements.

The Molar Volume. Since we have decided on 32 as the *molecular* weight of oxygen, it might be useful to know what volume the formula weight of 32 g. would occupy. One liter of oxygen at 0°C . and 760 mm. weighs 1.429 g., so $\frac{32}{1.429} = 22.4$, the number of liters occupied by 32 g. of oxygen. We can, for convenience, imagine a box holding exactly 22.4 liters (Fig. 64).

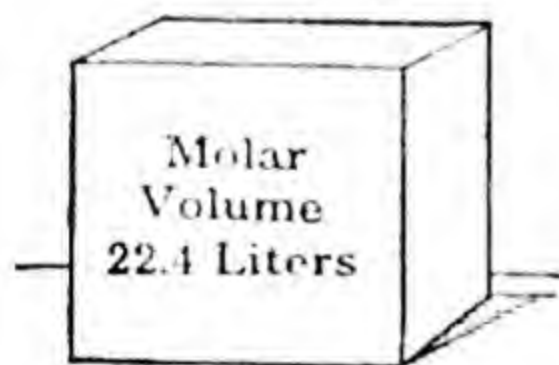


Fig. 64. Molar volume of gases.

This is nearly one cubic foot. If it is filled with oxygen or any other gas under standard conditions, the weight of the contents in grams must be the *formula weight* of that gas, since that is true for oxygen. By Avogadro's Law this box must hold the same number of molecules of any gas, so the weights vary as the weights of single molecules. The contents of the box filled with

hydrogen weigh 2.016 g., therefore the molecular weight of hydrogen is 2.016. The molar volume of methane, CH_4 , weighs 16.04 g., so the molecular weight is 16.04.

The volume occupied by one gram molecular weight of any gas at 0° C. and 760 mm. pressure is 22.4 liters.

In actual practice we should find it awkward to weigh 22.4 liters. We should simply weigh (get the density of) any convenient volume, perhaps 200 ml., and calculate the weight of 22.4 liters, as measured at 0° and 760 mm.

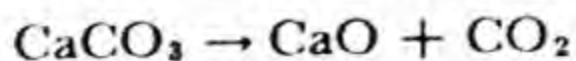
There are 6.03×10^{23} molecules of any gas (standard conditions) in 22.4 liters. This is *Avogadro's Number*. Since there are 6.03×10^{23} molecules in 44 g. of CO₂, carbon dioxide, the actual weight of one molecule is apparent.

NOTE: The weight of one liter of any gas in grams can be calculated in a moment by dividing its molecular weight by 22.4. For example, 22.4 l. of oxygen (G. M. V.) weigh 32 g. Therefore 1 liter weighs $\frac{32}{22.4} = 1.429$ g.

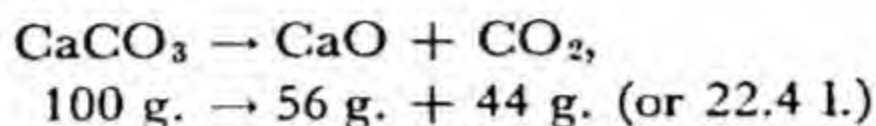
2. What is the molecular weight of a gas 500 ml. of which weigh 0.235 g. under standard conditions?
3. A bulb of 300 ml. volume was filled with vapor from an easily volatilized liquid at 45°. The barometer read 740 mm. What was the molecular weight of the substance if the gas weighed 2.25 g.?
4. Calculate the weight of 1 liter of nitrogen (N₂); of 300 ml. of chlorine (Cl₂); of 1500 ml. of ammonia (NH₃).

The molecules of most, but not all, *elementary* gases are diatomic. For example, a molecule of chlorine is Cl₂ and of nitrogen N₂. Yet mercury vapor is monatomic and its *molecular* formula is Hg. Zn is the molecular formula for zinc vapor. The rare gases, such as helium, neon, and argon, are monatomic. Temperature affects some molecular structures to a marked degree. At 448° I₂ is the correct formula of iodine vapor, but at 1700° iodine must be written I. At 193° sulfur vapors are represented by S₈, but at 1719° by S₂. At 193° the G. M. V. (22.4 liters) of sulfur vapor (corrected to 0° and 760 mm.) weighs 256 g. This means that the molecular weight at that temperature is 256. Since one sulfur atom weighs 32, there must be eight atoms in the molecule.

The use of molecular formulas may seem puzzling at first, but it soon becomes a real convenience. The following example will show this: when limestone is heated to white heat in the kiln it forms quicklime and carbon dioxide:



How many liters of carbon dioxide can be liberated from 25 g. of limestone? The answer is found at once. The formula CaCO_3 represents a definite quantity, the gram-molecular weight (one "mole") or 100 g. So does CO_2 represent one mole. But the molecular weight in grams of any gas occupies 22.4 liters. (See Molar Volume.) Now if 22.4 liters of carbon dioxide are released from 100 g. of limestone, 1 g. will release $\frac{22.4}{100}$ liters and 25 g. will release $\frac{25 \times 22.4}{100}$, or 5.6 liters.



The following calculation indicates application of this principle for atomic weight determination.

At 1 at. pressure 1 liter CO_2 weighs 1.9769 g.

At 0.5 at. pressure 2 liters CO_2 weigh 1.97014 g.

Carrying this idea of diminishing pressure farther (by extrapolation) we might approach the condition of an "ideal gas" in which the molecules are so far apart that intermolecular attractions and the volume-fraction occupied by the molecules themselves would be negligible.

On this basis

1 liter CO_2 should weigh 1.96327 g. and the G. M. V. of 22.414 liters should weigh 44.0047 g. The true molecular weight, obviously, is 44.0047 g.

Since the standard molecular weight of oxygen, O_2 , is 32 (and the atomic weight is 16) it is clear that

$$\begin{array}{rcl} \text{Mol. wt. of } \text{CO}_2 & = & 44.0047 \\ \text{Wt. of 2 atoms of O} & = & 32.000 \\ \hline \text{Wt. of 1 atom of C} & = & 12.0047 \end{array}$$

Chemical Methods of Determining Atomic Weights. Deviations from the gas laws (p. 71) make Avogadro's Law only a very good approximation. But equivalent weights (combining weights) may be determined with marvelous accuracy, as shown by the brilliant atomic weight determinations of the American chemist, T. W. Richards.

With the molecular weights of some compounds of a given element, correct analyses of those compounds, and the *exact*

equivalent weight of the element, it is not difficult to determine the *exact* atomic weight desired by use of the following law.

Law of Dulong and Petit. In 1818 Dulong and Petit observed that the product of the atomic weight of an element by its *specific heat* is equal to about 6.4 calories. (The specific heat of a substance is the number of calories required to raise the temperature of one gram 1° C. The specific heat of water is almost the highest of all, 1.0, while that of copper is 0.1.) The law does not hold accurately, but it is sufficient to settle many disputes, and invaluable in determining the atomic weight of an element which has no volatile compound. Use of this law in determining the atomic weight of silver is given below.

SPECIFIC HEATS

Al = 0.217	Pt = 0.032	B = 0.2518
Cu = 0.093	Ag = 0.056	C = 0.12
Pb = 0.031	Fe = 0.113	Si = 0.17
Ni = 0.109	Zn = 0.092	S = 0.17

sp. heat \times at. wt. = atomic heat		
Al, 0.217 \times 27	=	5.86
Cu, 0.093 \times 63.6	=	5.91
Ag, 0.056 \times 107.88	=	6.04

Equal numbers of atoms absorb equal amounts of heat, when raised 1° in temperature, so 1 g. of a heavier element with fewer atoms per gram must have a smaller heat capacity than 1 g. of a lighter element.

Analysis of silver oxide (93.1 per cent silver and 6.9 per cent oxygen) indicates that 215.76 g. of silver combine with 16 g. of oxygen or 107.88 g. with 8 g. Hence the combining weight of silver must be 107.88 g., accurately determined. As we have learned before, the atomic weight is either the same as the combining weight or some multiple of it, but this does not decide between such possible atomic weights as 107.88, 2×107.88 , 3×107.88 , etc. Dulong and Petit's Law, approximation though it is, makes the choice for us:

$$\begin{aligned} \text{Atomic weight of silver} \times 0.0558 &= 6.04 \\ \therefore \text{Atomic weight} &= 110, \text{ approximately} \end{aligned}$$

Obviously this indicates as atomic weight the value, 107.88 (the combining weight), rather than 215.76, etc.

Physical Methods of Determining Atomic Weights. Mass-spectrograph methods are so accurate that atomic weights are determined with an error of less than one part in 10,000.

In Fig. 65 is represented a vacuum tube with anode, and cathode perforated in the center. When a trace of some gas is admitted while a high potential electrical discharge takes place the high-speed electrons from the cathode knock electrons out of the gas molecules, thus forming positively charged gas ions.

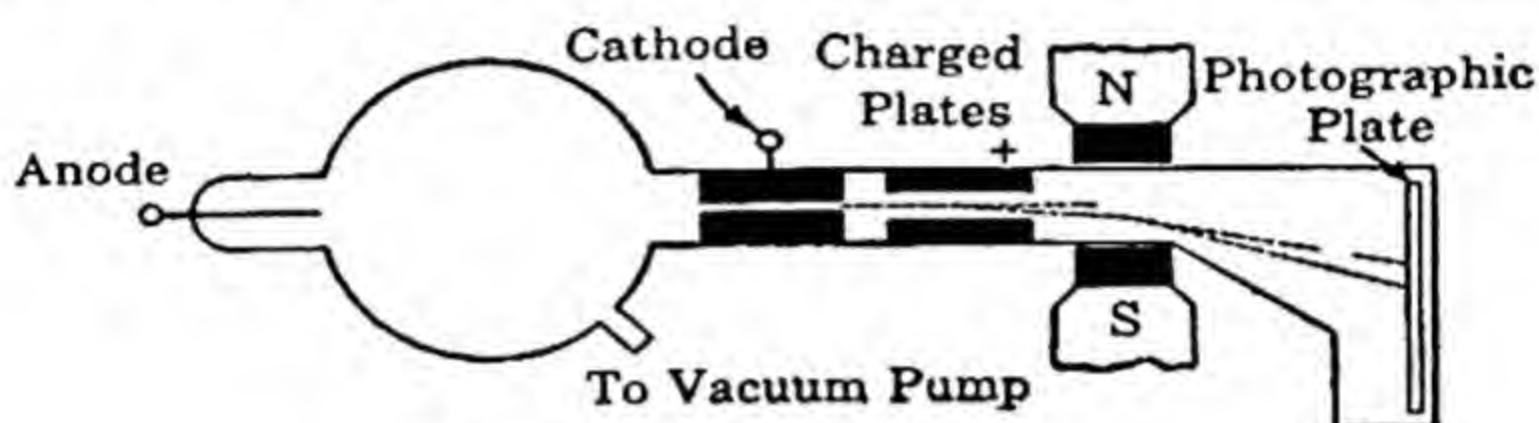


Fig. 65. Positive ray analysis.

Under the electrical stress these positive gas ions are driven toward the (negative) cathode, through the small center hole, and on to the photographic plate, where they produce an effect similar to that produced by light. Under the influence of a powerful electrical field and magnetic field NS these positive rays are bent out of their straight-line course according to the charge (readily calculated), speed, and mass. A selective velocity screen rejects all but a narrow band of velocities. Gaseous ions of equal mass are focused on the same line on the photographic plate, those of other masses on parallel lines. Hence it is possible to calculate, from the positions of these lines or bands, the relative masses of atoms.

Exercises

5. You have just discovered a new element, in fact found a 120-gram fragment of it in a mine. In an effort to determine its specific heat you heated the 120 grams to 100° (in a water bath) and quickly immersed the hot element in 500 grams of water at 20° . The beaker was well insulated, of course. The 500 grams of water rose in temperature to 22° C.
Calculate the specific heat and also the approximate atomic weight.

6. When 22.4 liters of water vapor (estimated under standard conditions) condense, how many milliliters of liquid water are formed?
7. Suppose you are so fortunate as to discover a new metal in the heart of a rock. It turns out to be moderately active chemically. How would you determine its atomic weight?
8. Could you calculate molecular weights (with H_2 as a standard of comparison) of NH_3 , HCl , and other gases by the time required for one liter of each gas to diffuse at constant pressure and temperature through a small hole, say 0.015 of an inch in diameter?
9. Does the molar volume of water (weighing 18 g.) refer to liquid or gaseous water? The molar volume is nearly one cubic foot.
10. If 1 liter of nitrogen at $0^\circ C.$ and 760 mm. weighs 1.251 g., what must be the molecular weight?
11. Find the molecular weight of a gas, of which 500 ml. at 18° and 752 mm. weigh 2.5 g.
12. The density of a gas is 2.2 as compared with air = 1. What is its molecular weight?
13. What will be the volume occupied by 12 g. of carbon tetrachloride (molecular weight 153.84) in the vapor state at 0° and 760 mm.?
14. The specific heat of an element in the solid state is 0.245. Its chloride contains 25.54 per cent of the element and 74.46 per cent of chlorine. What is the atomic weight of the element? (Hint: Calculate the approximate atomic weight by the rule of Dulong and Petit. Then calculate weight of element combined with 35.46 g., the equivalent weight, of chloride.)
15. How did we learn that S_2Cl_2 , and not SCl , is the correct formula of sulfur monochloride?

References

- "Molecular Weights by the Isotonic Method," *J. Chem. Ind.*, 56, 999 (1937).
 Sunier, A. A., "Some Methods of Determining Avogadro's Number." *J. Chem. Education*, 6, 299 (1929).

Chapter 14 SOLUTIONS

A solid and a liquid may be so intimately mixed that separate particles of the solid are no longer seen. With certain reservations, to be given later, we may call this mixture a **solution**. Salt water is a good illustration. If the mixture is less intimate, so that minute particles of the solid may be seen with the microscope, we may call it a **suspension**. Two liquids may also mix so completely as to deserve the term **solution**. If less thoroughly mixed, minute droplets of one liquid suspended in the other may be seen, under proper conditions. Such a mixture is called an **emulsion**. Milk is an example.

True solutions are non-settling and are homogeneous to the eye. Suspensions or emulsions settle, sooner or later, and are not homogeneous under severe optical tests. In a true solution the particles of dissolved substance are single molecules or, at most, groups of a few molecules. Consequently **a solution is a homogeneous molecular mixture of substances**. It should be noted that the proportions of the components of a solution (sugar and water, for example) may be varied, usually within limits. This distinguishes a solution from a compound.

Colloid Solutions. As just stated, true solutions are approximately molecular dispersions of substances in others. Dispersions of molecular aggregates larger than the largest single molecules now known, and yet not greater in the smallest dimension than approximately 200 millionths of a millimeter, are termed **colloid dispersions** or solutions. Coarse suspensions settle quickly, but some colloid solutions in water have failed to settle after many

years. Red colloidal dispersions of metallic gold in water have been prepared and kept for long periods of time.

Types of Solution. We are most familiar with solutions of solids in liquids, but liquids and gases may also be dispersed in liquids to form solutions. When a beaker of tap water is warmed, bubbles of dissolved air may be obtained. Furthermore, solids dissolve in solids and liquids dissolve in solids. Some alloys are mixtures of metals or compounds so intimate as to deserve the name *solid solution*.

We may add that gases dissolve in solids. Palladium under certain conditions dissolves over eight hundred volumes of hydrogen.

Some substances dissolve quite simply; others first react with the solvent to form soluble compounds, which then dissolve. Zinc does not really "dissolve in dilute sulfuric acid" but is converted into zinc sulfate, which dissolves. Calcium carbonate does not actually dissolve in hydrochloric acid but the calcium chloride that is formed does dissolve.

Exercise

1. To which type of solution does dilute sulfuric acid belong? Ordinary hydrochloric acid from the desk bottle? Ammonia water? Whiskey? Vinegar?

Water is the great solvent, but alcohol, ether, benzene, carbon disulfide, and thousands of other liquids are solvents for various substances. Water does not dissolve fats, yet carbon disulfide does.

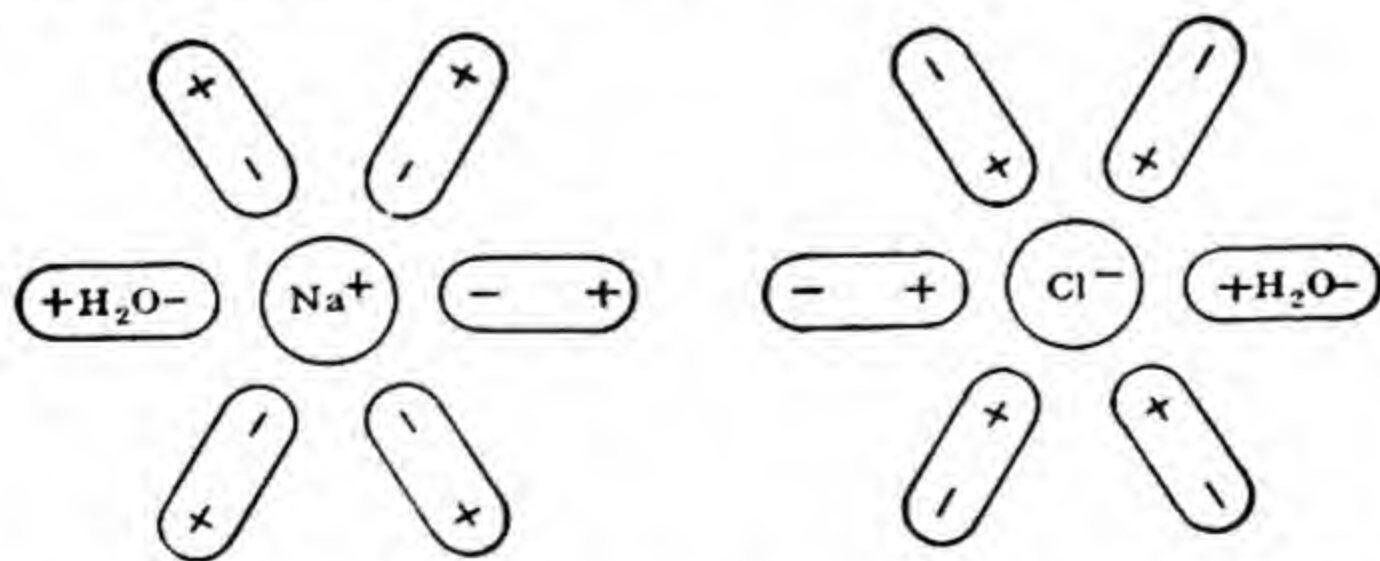


Fig. 66. In solution the positive Na^+ ion attracts the negative end of the dipolar water molecule while the negative Cl^- ion attracts the positive end. The ions are hydrated.

Sulfur dissolves readily in carbon disulfide, but not in water. Salts usually dissolve in other melted salts.

Covalent molecules are said to be electric dipoles when they possess two equal electric charges of opposite sign separated by a definite distance, reminding us of a bar magnet. The dipole moment is a product of charge by separation distance.

Some covalent molecules show polarity because they are unsymmetrical. Water is an example with its unsymmetrical structure, $\text{H} : \ddot{\text{O}} :$



In molecules such as $\text{H} : \text{H}$ or $\text{Cl} : \text{Cl}$ there is zero moment because the atoms are alike with equal radii. In anhydrous HCl the linkage is covalent but the electron pair is not shared equally — the hydrogen atom has less and the chlorine atom more of the negative electricity — due to the fact that the pair of shared electrons in the outer orbits is nearer to the positive nucleus of the atom having the smaller radius. Thus the molecule is a dipole as are the molecules of water, alcohol, liquid ammonia, liquid sulfur dioxide, acids, bases, and salts.

Such *polar molecules* tend to form chains, positive end attracting negative end, etc. Non-polar molecules (hydrocarbons, etc.) are squeezed out and so in general polar liquids mix, more or less, with polar liquids. The old saying had it, "oil and water do not mix." On the theory that "like loves like" the strongly polar acids, bases, and salts are more likely to dissolve in water than in benzene, C_6H_6 . On the other hand fats (almost non-polar) and rubber dissolve in benzene but not in water. Of course there are degrees of polarity and some substances are "slightly polar," etc.

The addition of a liquid of intermediate polarity, or one containing both a polar and a non-polar molecular region, such as alcohol, increases the miscibility of a polar liquid, such as water, with a non-polar liquid, such as hexane or benzene. Many other examples might be given were it necessary to do so.

The mutual attraction of polar molecules in a liquid gives abnormally high boiling points for the size of the molecules. H_2 boils at -253° and O_2 at -183° yet their compound, H_2O , boils at 100° .

SOLUBILITY OF LIQUIDS IN WATER. PER CENT (BY WEIGHT)
AT 20°

	PER CENT		PER CENT
Benzene	0.057	Carbon disulfide	0.21
Nitrobenzene	0.19	Chloroform	0.80
Aniline	3.49	Ethyl acetate	7.9
Phenol	8.2	Ethyl alcohol	Unlimited
Carbon tetrachloride	0.08	n-Butyl alcohol	7.8
		Diethyl ether	4.6

Definitions. The liquid in which a solid or gas has been dispersed to form a solution is called the *solvent* and the substance dissolved the *solute*. In the case of two liquids or two solids, each one may be said to be dissolved in the other, though the one present in larger quantity is usually termed the solvent. A mixture of gases might be called almost a perfect solution.

By *concentration* we mean the amount of solute dissolved by a definite quantity of the solvent, often referred to as so many grams per 100 ml. of solvent (or even per 100 ml. of solution). A solution containing very little of the solute is *dilute*. In a *concentrated solution* there is a larger amount of dissolved substance. Solutions may be made more concentrated (up to a certain limit) by adding more solute (preferably finely powdered) and shaking or stirring for some time, or by evaporating a dilute solution to remove part of the volatile solvent. Carried to the limit this is *evaporating to dryness* (in the case of solids in liquids) and the solute is recovered as a dry solid.

It is often incorrectly stated by the student that a saturated solution is one that contains all it can hold of the dissolved substance. That this is an error is readily proved by the formation of *supersaturated* solutions. Stir powdered sodium sulfate ($\text{Na}_2\text{SO}_4 \cdot 10 \text{ H}_2\text{O}$) or even the anhydrous salt for some time in water at 30° C., making sure that some is left over. Let settle and decant most of the solution into a clean flask, taking care that no fragment of the solid is transferred. Cover the flask to keep out dust and let cool. Now this solution, saturated at 30° C., contained all it could hold, or it would have taken up more when it had the chance. After cooling to 15° the solution should throw down part of the solute because, in general, solids are less soluble on cooling. Yet this particular one continues to hold at 15° all it held at 30°. The same thing can be done with photographer's "hypo." We call the solution at 15° *supersaturated* and the natural definition — that it contains *more* than it can

hold — is absurd. But toss in a minute fragment of a crystal of sodium sulfate and quickly a beautiful network of crystals radiates from the fragment. The amount thus crystallizing out is the difference between the amounts securely held at 30° and 15° . We now see a more accurate definition.

A saturated solution is one which will remain unchanged in concentration if placed in contact with some of the undissolved solute. It is said

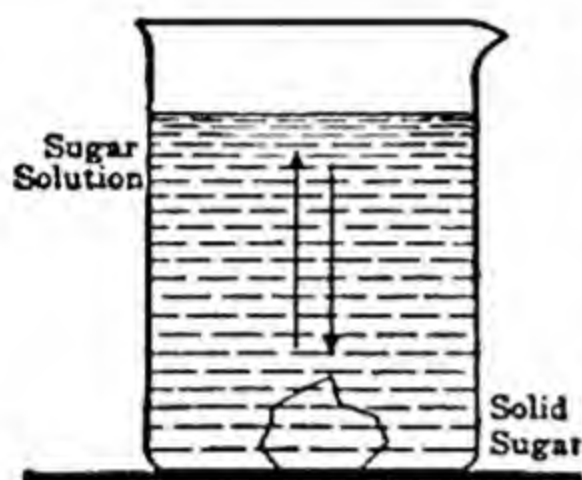


Fig. 67. Equilibrium in a saturated solution.

to be in equilibrium with excess of solute. That is, when we stir sugar, for example, into water, it continues to dissolve until the rate at which the sugar molecules in solution deposit on the lumps of solid sugar just equals the rate at which the solid throws molecules into the solution (Fig. 67). There is then no further change in the quantity in solution, but there is ceaseless activity. If a sugar crystal with a

corner broken off is put into the solution, it will be repaired without gain or loss in weight.

A supersaturated solution is in an unstable condition, and if placed in contact with some of the solid solute, it throws down the excess over the amount held by a saturated solution. Therefore it can be stated that a supersaturated solution has a higher concentration than the corresponding saturated solution.

An unsaturated solution has a lower concentration than the saturated solution.

2. If a clear solution of "hypo" ($\text{Na}_2\text{S}_2\text{O}_3$) were given you to test, how could you tell whether it was unsaturated, saturated, or supersaturated?

Water saturated with one substance may still dissolve another, just as a box of oranges may take up considerable sand and finally a surprising amount of water.

Measuring Solubility. There are many degrees of solubility. At room temperature limestone (CaCO_3), called calcium carbonate in its pure form, dissolves to the extent of 0.0013 g. in 100 ml. of water; but 143 g. of potassium hydroxide dissolve in the same quantity of water.

By a "10 per cent solution" we mean one containing 10 grams of solute and 90 grams of water (or solvent).

The *temperature effect* on solubility must be considered in any of these quantitative statements. Nearly all solids are more soluble with rise in temperature, but there are a few exceptions, notably some calcium salts of organic acids. (Gases, however, are less soluble with rise in temperature.) Potassium nitrate is seven times as soluble at 70°C. as at 8°C. There can be no accuracy, then, in a solubility statement unless the exact temperature of the measurement is given. This is usually 18°C. or 20°C.

To make a solubility measurement we merely determine the number of grams of solute taken up by 100 ml. of water in a saturated solution at a definite temperature. This may be done by adding an excess and, after much stirring and settling, removing an accurately weighed or measured portion of the clear solution and carefully evaporating it to dryness on a steam bath. The loss in weight represents the water and the residue the solute. The results can be calculated as grams per 100 ml. of water (or 100 ml. of solution if preferred). Less time is required if one heats an excess of solid with water at a higher temperature than the one at which the measurement is to be made. The solution is then cooled and held a short time at the exact temperature desired until the excess has deposited and settled. A measured portion is then evaporated to dryness as before.

The solubilities at various temperatures may be plotted in the form of curves, using the ordinates to represent the number of grams of solid dissolved by 100 ml. of water. The abscissas represent temperatures.

Solubility and rate of solution are not synonymous.

With the curves in Fig. 68 the solubility at any temperature may be read at a glance. What is the solubility at 18°C. and 90°C. of lead nitrate? Of sodium chloride at 77°C. ?

3. Plot points on a solubility diagram according to the following approximate data and then connect these points in smooth curves (or straight lines, as the case may be).

	0°	10°	30°	50°	70°	90°	100°
Potassium alum	6.5 g.	8.0 g.	17.5 g.	32.0 g.	113.0 g.		
Ammonium chloride	29.0 g.	33.0 g.	42.0 g.	50.0 g.	60.0 g.	72.0 g.	78.0 g.

Cerous sulfate is much more soluble in cold water than in hot. As a lecture experiment a solution saturated at 20°C . may be heated to 100°C . when three-fourths of the total will form a solid mass of crystals. For preparation of this salt see *J. Chem. Ed.*, 14, 315 (1937).

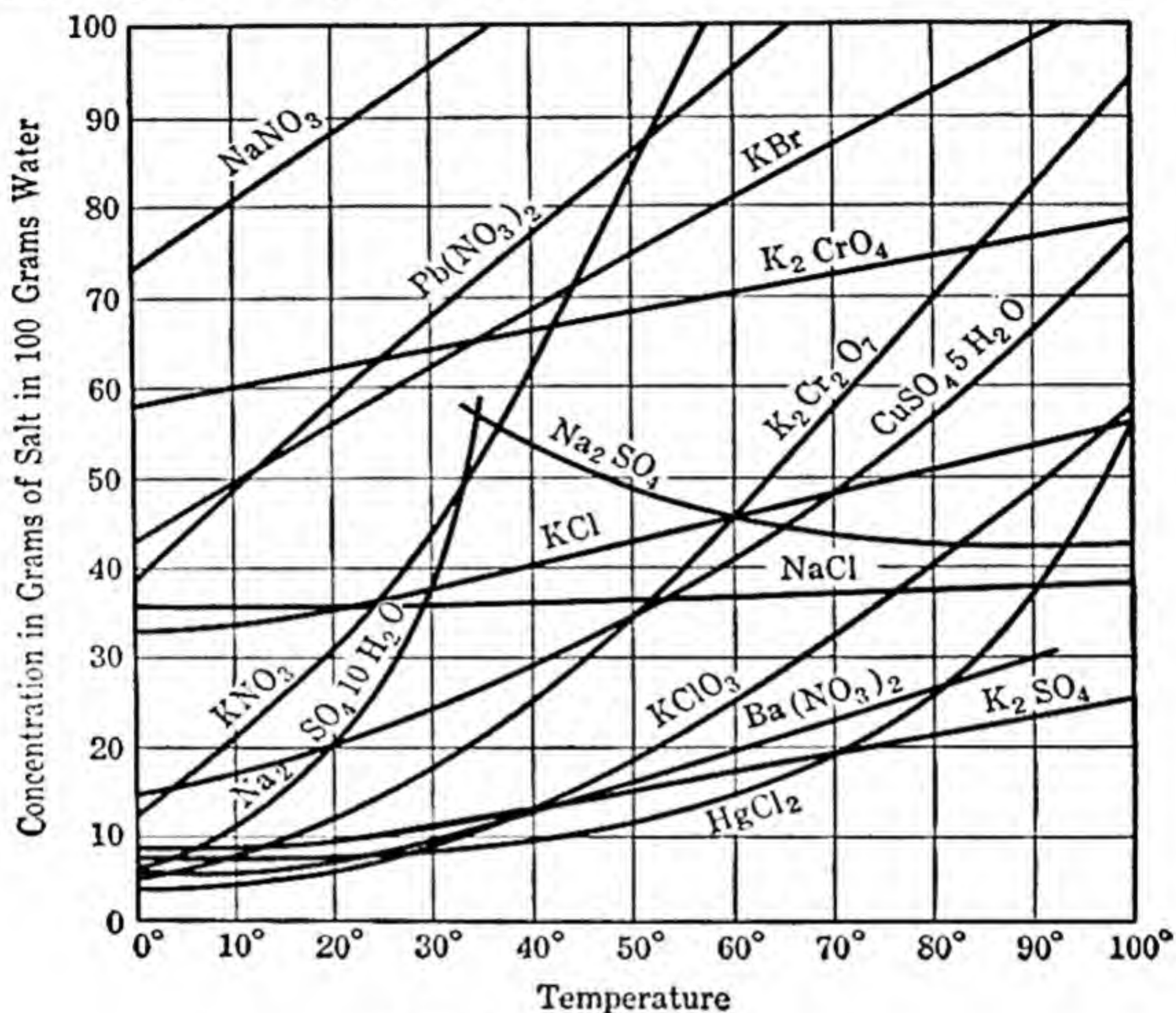
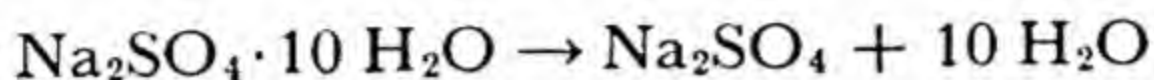


Fig. 68. Solubility chart.

Heats of Solutions. One gram molecular weight of concentrated sulfuric acid added to a large volume of water releases 39,170 cal. On the other hand, one gram molecular weight of ammonium chloride *absorbs* 3880 cal. on dissolving. Many salts produce this cooling effect or, in other words, their heat of solution is negative. This cooling effect may depend upon changes in the aggregation of water molecules caused by the dissolved substance. Conversely when these salts crystallize from solution heat is given out. When sodium acetate crystallizes from a supersaturated solution, much heat is released. This fact is utilized in one type of hot-water bottle useful for travelers, although a more common type depends upon the oxidation of moist iron powder.

Breaks in Solubility Curves. Transition Points. Referring to Fig. 68, the chart of solubility curves, we observe a peculiar break, or sharp peak, in the curve for sodium sulfate. Using $\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$, we find that its solubility increases up to 32.4° and then suddenly decreases. The fact is that at 32.4° this hydrate loses its water of hydration:



Above 32.4° the curve represents the solubility of anhydrous sodium sulfate, Na_2SO_4 , this salt being less soluble with rise in temperature. In other words this sharp point is the intersection of the two curves for these two crystalline forms of sodium sulfate. Such points, or temperatures, are called *transition points* and represent a distinct physical change (sometimes chemical also).

4. If you were in a hurry to dissolve some sodium chloride, would you use hot or cold water?
5. Salt solutions are heavier than water. To dissolve commercial quantities of some solid substance without the expense of stirring or heating, would it be better to place the solid at the bottom of the vat or on a perforated shelf near the top?

Solubility of Liquids in Liquids. Many pairs of liquids mix (dissolve in each other) in all proportions. Water and alcohol, water and sulfuric acid, water and glycerine are examples. But "oil" and water do not mix at all. It is true that an emulsion of minute droplets of oils in water can be made, but these droplets contain thousands of molecules and so are not in true solution. Other liquids dissolve in each other to a limited extent. If ether and water are shaken and allowed to stand, an ether layer rises to the top with a water layer beneath. Analysis shows the presence of a little water dissolved in the ether layer and a little ether dissolved in the water layer.

Benzene, C_6H_6 , dissolves but little more than a trace of water (only 0.57 g. in 1000 g. of benzene), yet in some research work it is advisable to dry the benzene with metallic sodium (safe with *traces* of water), with activated aluminum oxide, or with "silica

gel." From these illustrations we see that liquids may be *completely miscible*, *partially miscible*, or *immiscible*.

6. Give an illustration of each type.

Critical Solution Temperature. Certain liquids immiscible at room temperature may form a homogeneous solution when heated to a "critical solution temperature." A mixture of 2 ml. of anhydrous ethanol and 4 ml. of bicyclohexyl exhibits a critical solution temperature of $23.4^{\circ}\text{C}.$; with 1 per cent of water present, this temperature becomes 41.4° , and with 2 per cent water 54.1° . Thus the critical solution temperature can be plotted against the percentage of water present and the resulting curve used for determining the water content of high-proof alcohol of unknown concentration.

If to a water solution of some substances a liquid miscible with water, but not itself a solvent for those substances, is added, nearly all of the solute may be precipitated. Acetone added to a water solution of ferrous sulfate, FeSO_4 is an example.

Solubility of Gases in Liquids. Henry's Law. In 1803 Henry observed that at any definite temperature *the solubility by weight of a gas in a liquid is proportional to the pressure* of the gas. Ammonia (NH_3) at 0° and 760 mm. dissolves to the extent of 114,800 ml. in 100 ml. of water, but its solubility does not follow Henry's Law. In fact, all very soluble gases are exceptions, probably because they react to some extent with water.

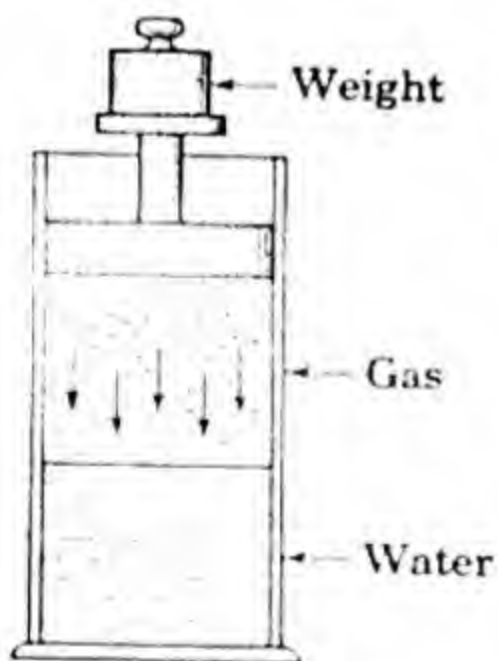


Fig. 69. The solubility by weight of a gas in a liquid is proportional to the pressure of the gas.

A saturated solution of carbon dioxide contains 5.5 g. per liter at room temperature and standard pressure.

With rise in temperature all gases are less soluble in liquids. Warming ammonia water drives off much of the dissolved gas and boiling removes it all. Passing a stream of another gas, say air or steam, through a solution of a gas in water removes the dissolved gas for reasons given in the next section.

7. Would Henry's Law hold closely for the solubility of the very soluble hydrogen chloride in water? Of the slightly soluble nitrogen in water?

Law of Partial Pressures. If a liter of hydrogen and a liter of nitrogen at 760 mm. are forced together into a one-liter vessel, the total pressure becomes two atmospheres and each gas exerts its own part of the total pressure (one atmosphere).

Dalton in 1802 stated that *in a mixture of gases each gas exerts the same pressure as if it alone occupied the entire vessel and the total pressure is the sum of the partial pressures of the different gases.* Of course this law does not hold for gases that react with each other.

The natural consequence of this fact is that in a mixture of gases over a liquid each one dissolves according to its own partial pressure (see Henry's Law as well as Dalton's), independently of the presence and pressure of other gases. For example, air is a mixture of about four volumes of nitrogen and one of oxygen. At normal pressures (760 mm.) the oxygen is responsible for only 152 mm. of this pressure and nitrogen for the other four-fifths, or 608 mm. The oxygen of air dissolves in water to the exact extent that it would were the nitrogen not present. But if the nitrogen of our atmosphere suddenly ceased to exist, the oxygen remaining would exert a normal pressure of only 152 mm. and just as much of it would dissolve in rivers and lakes as at present. Oxygen at 760 mm. (five times its partial pressure in ordinary air) is five times as soluble in water as when found in air (when 760 mm. is the total pressure of nitrogen, oxygen, etc.).

If a gas, not very soluble in water, is bubbled through ammonia water, for example, much of the ammonia is removed because the stream of other gas (air,

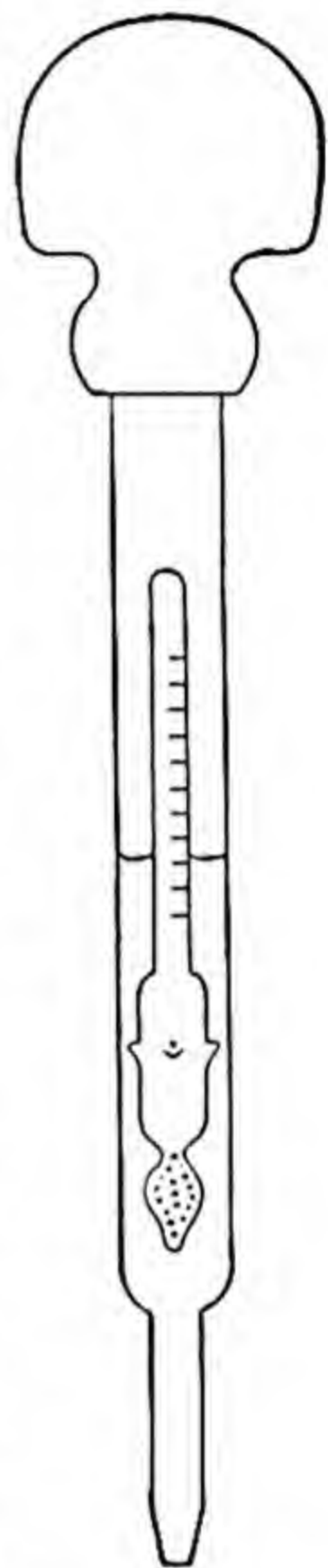


Fig. 70. Hydrometer for storage battery. The concentration of the sulfuric acid is determined by its density—and comparison with tables.

perhaps) sweeps away the ammonia gas just above the liquid and thus reduces its partial pressure in the air immediately above the liquid to nearly zero. Since the solubility of ammonia depends in part on its pressure as a gas above the liquid, it is evident that ammonia will, under such conditions, pass continuously out of the liquid. This is really a steady disturbance of solution equilibrium. Air and steam are both used to remove volatile substances from solution. In boiling ammonia water the escape of steam bubbles does much the same thing as if a stream of steam were led into the solution from outside.

8. How could you increase the solubility of carbon dioxide in water? How decrease it? Explain the effervescence of soda water.

Distribution Law. In the chapter on the halogens some mention is made of the very slight solubility of iodine in water (0.034 g. per liter) and its great solubility in carbon disulfide. A dilute

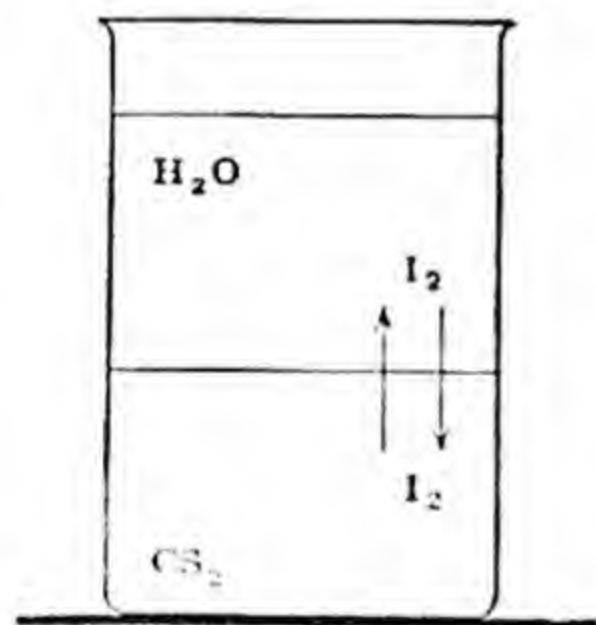


Fig. 71. Distribution of iodine between two solvents.

solution of iodine in carbon disulfide has a beautiful violet color. At greater concentrations the solution is almost black. If we shake a small crystal of iodine with water until the water is saturated, filter the solution and then add carbon disulfide to the filtrate, and shake the mixture, we observe a violet color in the heavy carbon disulfide layer. Most of the iodine has been *extracted* from the aqueous solution by the carbon disulfide, in which it is far more soluble. In fact the iodine is present in a milliliter of each of the

two solvents in the exact ratio of its solubilities in them. If it is one thousand times as soluble in carbon disulfide as in water, only one part will remain in each ml. of water for every one thousand parts in each ml. of carbon disulfide. The dissolved iodine is in constant motion, passing from one liquid to the other, as indicated by the following equilibrium:



This equilibrium can be disturbed by adding something that reacts with the iodine in the water layer. Sodium thiosulfate ("hypo") or even sodium hydroxide will do this. As fast as the very small amount of iodine left in the water is used up, more replaces it from the carbon disulfide, and finally, after sufficient additions and shaking, all the iodine is removed from the carbon disulfide, as shown by the complete loss of violet color. Iodine is 85 times as soluble in carbon tetrachloride as in water.

Hydrotropic Solutions are those aqueous salt solutions which effect decidedly greater solubility of slightly soluble substances than does pure water at the same temperature. Strong solutions of potassium iodide dissolve up to eight atoms of iodine for each atom of potassium. For many slightly soluble organic compounds an aqueous solution of sodium xylenesulfonate (rather concentrated) is an excellent solvent. Some salts exert the opposite effect — "salting out" dissolved materials.

Chapter 15 SOLUTIONS (continued)

Equivalent Weights. The weights of substances that react with each other in some definite proportion are chemically equivalent.

With this in mind, a glance at page 105 of the Valence chapter will show us that 1.008 g. of hydrogen, 23 g. of sodium, and 35.46 g. of chlorine are equivalent to each other in reactions or in compounds. Also one-half of a gram-atomic weight of magnesium and one-third of a gram-atomic weight of aluminum are equivalent to 1.008 g. of hydrogen or 35.46 g. of chlorine.

A Gram-Equivalent Weight	{	Of Hydrogen is 1.008 g. Of Oxygen is 8 g. Of any Acid contains 1.008 g. acidic hydrogen Of any Base contains 17.008 g. of basic hydroxyl Of any Salt contains one gram equivalent of the metal, or positive group
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Thus 36.468 g. of HCl is the equivalent weight because it contains 1.008 g. of acidic hydrogen; 40.008 g. of NaOH the equivalent weight because it contains 17.008 g. of basic hydroxide groups; and 58.46 g. of NaCl the equivalent weight because it contains 23 g. of sodium.

By acidic hydrogen is meant the hydrogen atoms in acids displaceable by a metal in contrast to hydrogen atoms in sugar, starch, etc., which are not so displaced.

Normal Solutions. *A normal solution of an acid, base, or salt contains one gram-equivalent weight of the solute in one liter of solution.*

Hence, to make a normal solution of hydrogen chloride we need dissolve one formula weight (36.468 g.) in one liter of solution, but in the case of H_2SO_4 the entire formula weight (98 g.) is too much — we use only half the formula weight in a liter of solution, because of the two replaceable hydrogen atoms in the H_2SO_4 molecule. Of H_3PO_4 we use one-third the formula weight. Obviously a normal solution of copper sulfate must contain in one liter an equivalent weight of combined copper ($\frac{1}{2}$ of 63.54 g.). In actual practice the common blue hydrate, $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$, would be weighed out so the molecular weight should include the water of crystallization.

One formula weight of $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ is

$$\begin{array}{ccccccc} \text{Cu} & & \text{S} & & 4 \text{ O} & & 5 \text{ H}_2\text{O} \\ 63.54 & + & 32.066 & + & 64 & + & 5 \times 18.016 = 249.686 \text{ g.} \end{array}$$

One equivalent weight of "blue vitriol" is $\frac{249.686}{2} \text{ g.} = 124.843 \text{ g.}$

A normal solution contains 124.843 g. of the blue crystals in 1000 ml. of **solution**.

The symbol for normal is N. Twice normal is 2 N and tenth normal 0.1 N or N/10.

The term "equivalent weight" has another meaning when applied to an oxidizing or reducing substance.

Exercises

1. How could you make one liter of a normal solution of hydrobromic acid (HBr)? Of potassium hydroxide? Of barium hydroxide, $\text{Ba}(\text{OH})_2$?
2. How many grams of $\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$ are there in 800 ml. of N/5 solution? Of Na_2SO_4 in 800 ml. of N/5 solution?
3. Define equivalent weights of acids, bases, and salts.
4. Two beakers containing dilute and concentrated sugar solutions are kept under a bell jar. Explain concentration changes.

To be exact we must state that solutions may be normal with respect to the ion considered. For example, a molar solution of KHSO_4 is 1 N for the K^+ ion, 1 N for the H^+ , but 2 N for the SO_4^{2-} ion.

Molar Solutions. *A molar solution contains a molecular weight in grams (one mole) of solute in a liter of solution.* Since the molecular weight of sulfuric acid is 98.026, a molar solution of this acid contains 98.026 g. per liter. Note that we did not refer to 1000 ml. of solvent, but to 1000 ml. of solution, a very different thing. A molar solution of sodium chloride contains 58.46 g. per liter of solution.

A *molal solution* contains 1 mole of solute in 1000 g. of solvent, while a *molar solution* contains 1 mole in 1 liter of solution. Both terms have convenience in use. One mole is the same as one formula weight in grams.

5. How could you make 400 ml. of molar copper sulfate solution? Remember that the "blue vitriol" used is $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$.
6. How could you make one-tenth molar potassium nitrate?

Freezing-Point Lowering. The fact that salt water freezes at a lower temperature than pure water has long been known. Cavendish's secretary, Blagden, observed that the amount of this lowering of the freezing point is proportional to the concentration of dissolved substance. For example, if a solution of 10 g. of glycerine in 1000 g. of water freezes at a fraction of a degree below zero, then a solution of 20 g. of glycerine per 1000 g. of water must freeze twice as far below zero and a 50-g. solution five times as far below zero. A most interesting point is brought out if solutions of gram-molecular weights of such substances as alcohol, glycerine, sugar, and acetone, in 1000 g. of water, are frozen. They all freeze at about -1.86°C . Hence *the molal depression of the freezing point of water is 1.86°* . We can obtain the molecular weight of a soluble substance by noting how many grams of it must be dissolved in 1000 g. of water to lower the freezing point to -1.86° . If 80 g. are required, 80 is, of course, the molecular weight. If, in another instance, a solution freezes at -0.186° , the lowering is only one-tenth that produced by a molar weight, and hence the weight of solute used per 1000 g. of water is only one-tenth the molecular weight.

A solution of 46 g. of ethyl alcohol ($\text{C}_2\text{H}_5\text{OH}$) in 1000 g. of water freezes at -1.86° , as do solutions of 1000 g. of water con-

taining 342 g. of cane sugar ($C_{12}H_{22}O_{11}$) or 32 g. of methyl alcohol (CH_3OH). These are all gram-molecular weights. An important exception to these statements must be made for acids, bases, and salts. They will be discussed later.

7. If a solution made by dissolving 14 g. of a substance in 100 g. of water freezes at -0.4° , what is the molecular weight of the substance?

In calculating the molecular weight of a substance soluble in water the following proportion will be found useful:

$$\begin{array}{l} \text{Observed lowering} : 1.86^\circ = \text{grams of solute in 1000 g.} \\ \text{solvent} : \text{mol. weight of solute} \end{array}$$

MOLECULAR LOWERING OF FREEZING POINT AND MOLECULAR RISE OF THE BOILING POINT OF SOLVENTS

SOLVENT	PURE SOLVENT FREEZES AT	MOLEC. LOW. OF FREEZ-ING PT.	PURE SOLVENT BOILS AT	MOLEC. RISE OF BOILING PT.
Water	0°	1.86°	$+100.0^\circ$	0.52°
Carbon tetrachloride (CCl_4)	-24.7°	2.98°	$+78.5^\circ$	4.88°
Benzene (C_6H_6)	$+5.5^\circ$	5.12°	$+80.2^\circ$	2.57°
Phenol (C_6H_5OH)	$+40.0^\circ$	7.27°	$+182.1^\circ$	3.60°

For the anti-freeze solution in your car alcohol or glycol, $C_2H_4(OH)_2$, usually is used, dissolved in water.

A melted mixture of 40 per cent $NaNO_2$, 53 per cent KNO_3 , and 7 per cent $NaNO_3$ freezes and melts at $288^\circ F$. It is much used as a standard heat-transfer liquid in industry (cheaper than mercury).

8. A 30 per cent (by weight) solution of denatured alcohol freezes at $-0.2^\circ F$. and a similar concentration of glycol ("prestone") freezes at $+7.7^\circ F$. Which do you prefer for your car radiator if costs were equal? Alcohol is much more volatile.
9. How much should 8.5 g. of naphthalene ($C_{10}H_8$) in 208 g. of benzene lower the freezing point?

Boiling-Point Rise and Vapor Tension. The work of Raoult on freezing-point lowering was applied (1882) to a study of the effect of dissolved substances on vapor tension. A non-volatile solute interferes with the evaporation of a solvent by getting in the way of and attracting escaping molecules, thus lowering the

vapor tension of the solvent. Consequently the solution must be made hotter to produce a vapor tension just equal to the pressure of the atmosphere; that is, to make the liquid boil at 760 mm.

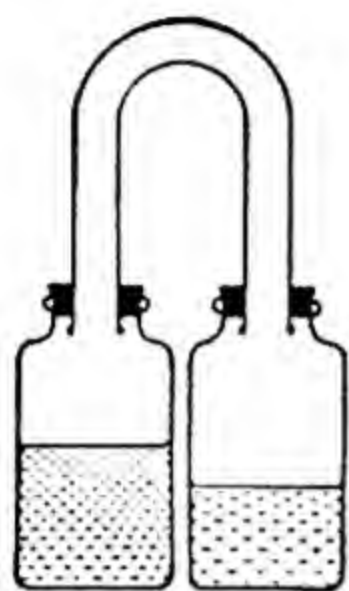


Fig. 72. What will occur if a bottle of water and a bottle of sugar solution are connected as shown here?

Water boils at 100°C ., but Raoult found that if a molecular weight in grams of any comparatively non-volatile substance (except acids, bases, and salts) is dissolved in 1000 ml. of water, the solution boils at 100.52°C . The boiling-point rise is 0.52°C . Obviously the molecular weight of such a substance as glycerine or sugar may be obtained by measuring the boiling point of any convenient solution and from this calculating how many grams of solute would be required to raise the boiling point 0.52°C . To sum up, the lowering of the vapor tension of a solvent (and the consequent rise in boiling point) caused by dissolved substances other than acids, bases, and salts is directly proportional to the molecular concentra-

tion of the solute. *The boiling-point rise caused by one formula weight in grams of solute per 1000 grams of solvent is 0.52° for water, 1.67° for acetone, and 2.57° for benzene.* Raoult's Law does not hold where there is reaction between solute and solvent.

10. What should be the boiling point of a solution containing 95 g. of cane sugar ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$) in 500 ml. of water?
11. A solution of 40 g. of AB in 1000 g. of benzene freezes at -1.2°C . Benzene freezes at 5.5° . What is the molecular weight of AB?

There are some very soluble substances, such as calcium chloride, which become wet in ordinary air. Such substances are *deliquescent*. They dissolve in the film of moisture on their surface, forming a concentrated solution with a vapor tension lower than the vapor pressure of the air. Consequently moisture is deposited in the solution, tending to dilute it. This explains the use of anhydrous calcium chloride as a drying agent to take up moisture from gases. The mere fact that the vapor pressure of water in ordinary air may be greater than the aqueous tension of some crystals is not enough to account for deliquescence; other-

wise water from the air would continue to condense on powdered diamonds or sand.

Such extremely soluble substances as glycerine, glycol, sugars, and sorbitol (a recent commercial product), when added in small amounts, have the valuable property of keeping sufficiently moist tobacco, cellophane, textiles, leather, and glue.

Osmotic Pressure. The walls of plant cells, bladder tissue, parchment paper, and many other membranes are *semipermeable*. They permit the diffusion of water while checking or prohibiting the passage of certain dissolved substances.

Osmosis is the selective flow of solvent through a semipermeable membrane from a pure solvent into a solution or from a more dilute into a more concentrated solution.

In Fig. 73 we represent a simple device for demonstrating osmotic pressure which is, however, too crude for accurate quantitative study. A "thimble" of wet parchment paper filled with a concentrated sugar solution is attached tightly to a rubber stopper containing a long section of small glass tubing. The tube is firmly fixed in a vertical position in a beaker of pure water. After a few hours the level of the liquid in the narrow stem (marked with a label) has risen to a considerable height — to such height that *the weight of the column of liquid just equals the osmotic pressure of the solution*.

The pure water passes through the membrane (slowly) in both directions, but passes into the solution faster than it passes out. The result is an increase in the volume of liquid in the bulb shown by a rise in the narrow tube. The pressure set up is measured by the weight of the column of solution.

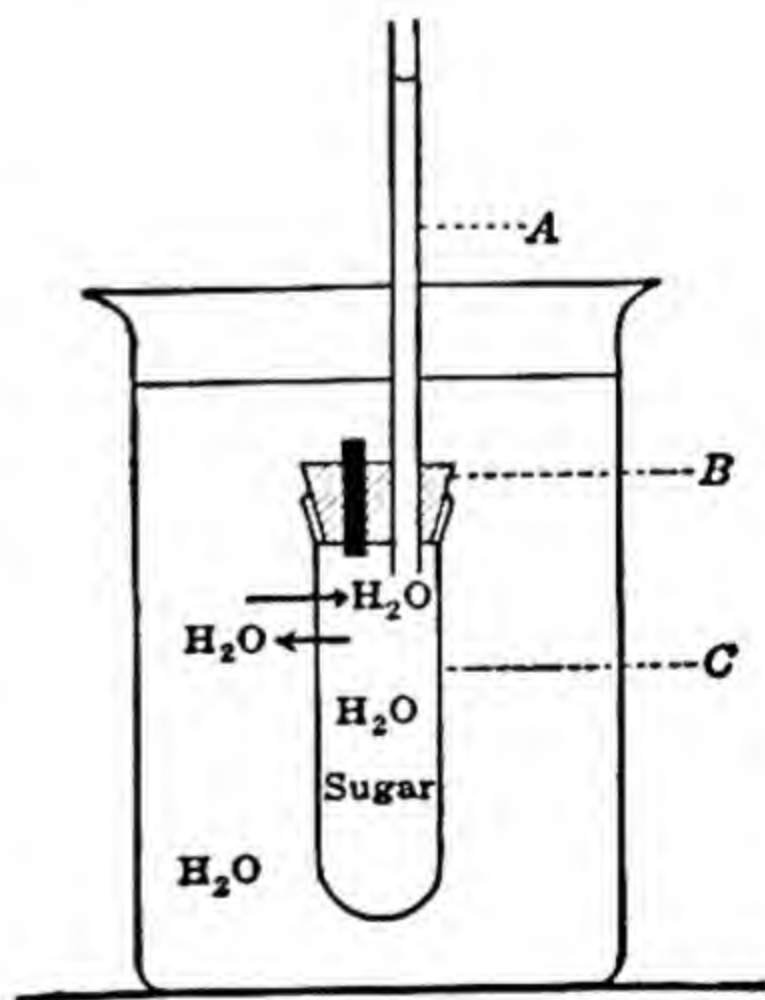


Fig. 73. Osmotic pressure cell with parchment cup membrane.

A carrot makes an excellent osmotic cup when hollowed out with a cork borer. After filling with sugar solution and fitting with a cork and glass tube, it is a wise precaution against leakage to bind adhesive tape tightly around the upper part of the carrot and over the stopper.

Osmotic pressure is the pressure required to stop the movement of solvent through a semipermeable membrane from a more dilute to a more concentrated solution.

Using solutions and pure solvents we find the *osmotic pressure is proportional to the concentration of the solute in the solution*. That is, a 10 per cent sugar solution has twice the osmotic pressure of a 5 per cent solution. If a more dilute solution is placed on one side of the membrane and a more concentrated on the other, the pressure will be proportional to the difference in concentration.

The osmotic pressure laws do not hold for acids, bases, and salts for very good reasons soon to be developed.

The preservative effect of sugar is said to be due largely to its effect on osmotic pressure. Microorganisms must have water for growth and if dehydrated by a concentrated sugar syrup (with osmotic pressure higher than that of the cell contents) they are killed. The tissues of the microorganisms may be considered as semipermeable membranes.

A spectacular experiment illustrating osmotic pressure as well as the formation of semipermeable membranes is easily performed. Crystals of salts of nickel, cobalt, copper, lead, manganese, and small lumps of ferric chloride may be dropped into ordinary commercial water glass (sodium silicate) diluted with two or three volumes of water. The fragment of nickel sulfate, for example, dissolving in the water of this solution reacts to form nickel silicate, a gelatinous material. This forms a sac, semipermeable in that it allows water to pass through in both directions but does not permit the molecules of nickel sulfate inside the sac to diffuse out. The concentration of the solution inside each little sac is greater than that outside because the fragment of crystal keeps it saturated. The result is shown by swelling and bursting of the sac. This lets out the contents, nickel sulfate, to react and form a new sac wall. Thus a tree-like growth upward (because of the lesser hydrostatic pressure above) appears with a startling rapidity in the case of ferric chloride and is quite appreciable in all cases. The "submarine forest" in many colors is worth observing for a day or so. The bursting of the sacs is a result of osmotic pressure of a more concentrated solution.

Exercises

12. State Henry's Law and give an illustration.
13. Solutions of equal osmotic pressures are called isotonic. Injections of fluid into our blood stream must be isotonic with the plasma (liquid portion of the blood). Why? A "physiologic salt solution," 0.9 per cent NaCl, is isotonic with the blood.
14. Hydrogen dissolves in palladium while nitrogen does not. If you sealed nitrogen in a thin-walled palladium tube and placed it in a flask of hydrogen what gaseous movements would you observe? Do you see any parallel to the osmotic pressure movement of solutions?
15. What do you mean by a gram-equivalent weight of hydrogen? Of sodium? Of magnesium? Of copper? Of aluminum? Of sodium chloride? Of sodium sulfate? Of sulfuric acid? Of aluminum sulfate? Of sodium hydroxide? Of barium hydroxide ($\text{Ba}(\text{OH})_2$)?
16. Why does a lump of anhydrous calcium chloride deliquesce in ordinary air while a diamond does not? Remember that a very thin (invisible) film of water may form on any solid surface exposed to ordinary air.
17. If you filled a bladder (semipermeable membrane) with a 0.2 M solution of sugar in water and placed it in a 0.1 M sugar solution, what would happen?
18. Prove that a solution is a mixture rather than a compound.
19. What weights of the following substances would be required to prepare one liter of normal solution: HCl, NaOH, H_3PO_4 , Na_2SO_4 , $\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$, $\text{BaCl}_2 \cdot 2 \text{H}_2\text{O}$, AlCl_3 ?
20. If 45 g. of a substance dissolved in 500 g. of water gives a solution boiling at 100.26° , what is the molecular weight of the substance?
21. If 140 g. of a substance dissolved in 2000 g. of water gives a solution freezing at -1.86° , what is the molecular weight of the substance?
22. How could you wash iodine out of carbon disulfide with water in spite of its vastly greater solubility in carbon disulfide?
23. The freezing point of milk is -0.56°C . How could you detect watering of milk?
24. Would an oyster look different if kept wet in fresh water (in storage) rather than in salt water? Why or why not?
25. What would happen to corpuscles if blood serum were replaced by water?
26. An auto radiator has a capacity of 12 liters. If you wished to fill it, or nearly so, with an aqueous solution of alcohol (ethyl) that would remain liquid at -20°C . what weights of alcohol and water would you use?

27. Millions of young plants are shipped with roots packed in moss wet with a glycerine-water solution. Why?
28. Compare efflorescence and deliquescence.

References

McKee, R. H., "Use of Hydrotropic Solutions in Industry," *Ind. Eng. Chem.* 38, 382 (1946).

Chapter 16 CHLORINE, BROMINE, IODINE, AND FLUORINE

The Halogen Family. Chlorine, bromine, iodine, and fluorine exhibit such close resemblances as elements and in their compounds that they are grouped as a family of "*halogens*." Of all the elements they are the least like the metals. The name *halogen* means "salt former," given because they all unite with metals to form salts, such as sodium chloride.

	AT. WT.	MELTING PT.	BOILING PT.	COLOR AND STATE
Fluorine (F)	19.00	-223°	-187.0°	Pale-yellow gas
Chlorine (Cl)	35.457	-101.6°	-34.6°	Greenish-yellow gas
Bromine (Br)	79.96	-72°	58.78°	Reddish-brown liquid
Iodine (I)	126.92	113.5°	184.4°	Violet-black solid

The iodine atom is the largest and fluorine the smallest of the halogens.

Radius of Ion in Crystals (Ångstrom units):

F	Cl	Br	I
1.36	1.81	1.95	2.16

CHLORINE

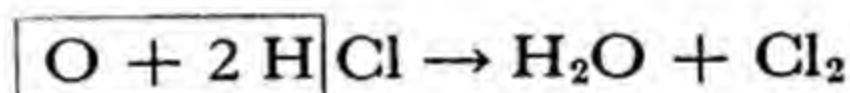
History. Chlorine was first prepared by Scheele in 1774 by the action of manganese dioxide on hydrochloric acid. However, it was thought to be a compound of hydrochloric acid and oxygen, even by Lavoisier. In 1810 Sir Humphry Davy tried in vain to reduce the supposed oxide and finally convinced the scientific world that this substance was really an element. He named it chlorine, from the Greek for "greenish-yellow."

Exercise

1. In what connection have we heard of Scheele before?

Occurrence. Chlorine is not found free in nature because it reacts so readily with many other substances, particularly metals. Its commonest compound is sodium chloride, common salt. This is found in sea water to the extent of nearly 3 per cent. Great Salt Lake contains 23 per cent. In some parts of the world salt is mined, and deposits are common. Potassium chloride is found in a large deposit at Stassfurt, Germany, associated with sodium chloride and magnesium chloride.

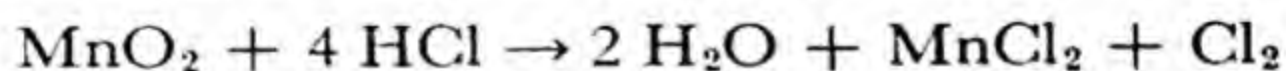
Preparation. The most convenient laboratory methods of preparation depend upon the oxidation of hydrogen chloride into water and free chlorine. The half molecule is used in the following equation for simplicity:



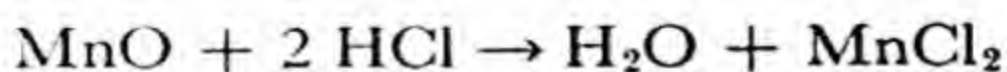
Oxygen alone does this only with extreme slowness unless aided by a catalyst at a favorable temperature. Good oxidizing agents such as potassium permanganate, manganese dioxide, sodium dichromate, and lead dioxide will oxidize hydrogen chloride rapidly without a catalyst.

Germany was found to have a commercial plant for the manufacture of chlorine based on the oxidation of HCl gas by oxygen as the mixture bubbled through a bath of melted anhydrous ferric chloride, FeCl_3 , and potassium chloride.

A concentrated solution of hydrogen chloride in water (called hydrochloric acid) is warmed (Fig. 74) with the oxidizing agent:



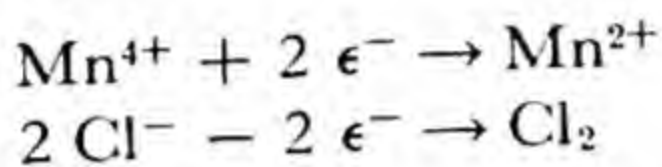
Had manganous oxide, MnO , been used no chlorine would have been released:



We may say that MnO_2 is an oxidizing agent and MnO is not, but this is only part of the truth. In MnO_2 the valence number of the metal is four, and in its product, MnCl_2 , the valence

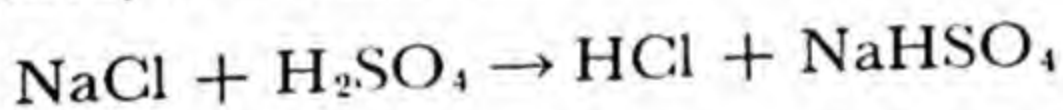
number has dropped to two. This fact introduces an extension of the idea of *oxidation* and *reduction*. A drop in valence number of the positive element or radical in a compound is reduction. The MnO_2 is *reduced* by the HCl (which also means that the MnO_2 oxidizes the HCl) because the manganese dropped in valence number from four to two. In the reaction with MnO the valence number of manganese is two and remains two in the product, MnCl_2 .

The half reactions are:



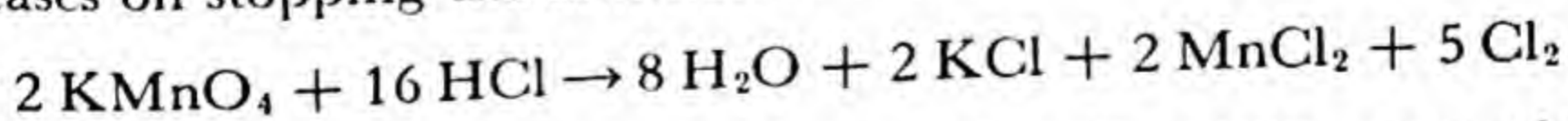
2. The reactions of hydrochloric acid with lead dioxide, PbO_2 , and lead monoxide, PbO , are similar to the above. Write the equations. Remember that the hydrogen of the acid unites with the oxygen of metallic oxides to form water.

In practice we generate the hydrochloric acid by the action of moderately diluted sulfuric acid on sodium chloride and oxidize it, as shown above, with manganese dioxide in the same operation



(Fig. 74). The gas is passed through a little water to remove hydrogen chloride and through concentrated sulfuric acid to dry it. It displaces air from the receiving cylinder.

Potassium permanganate is an excellent but expensive oxidizing agent for the purpose of making chlorine. Concentrated hydrochloric acid diluted with about one-third of its volume of water is dropped very slowly on the solid from a dropping funnel. The chlorine is released instantly without warming, and its flow ceases on stopping the addition of acid:



There is no valence change in the chlorine atoms appearing in 2MnCl_2 .

The electronic balancing of this equation is clear if we examine the products, H_2O , KCl , MnCl_2 , and Cl_2 , noting that some of the chlorine atoms still retain their negative valence number of

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one, while in the chlorine set free the valence number has changed from one negative to zero:

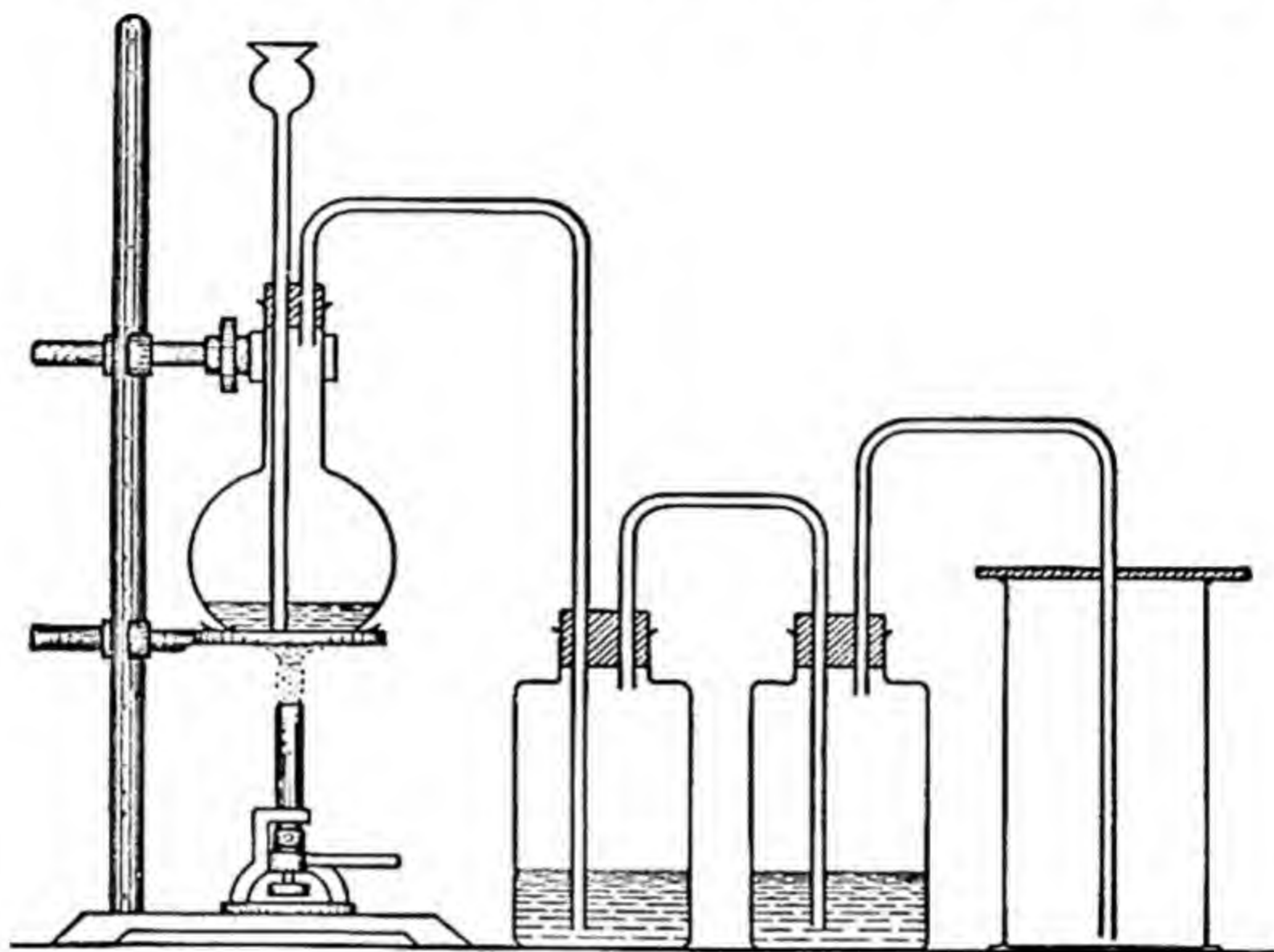
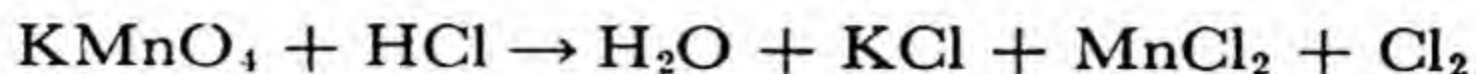
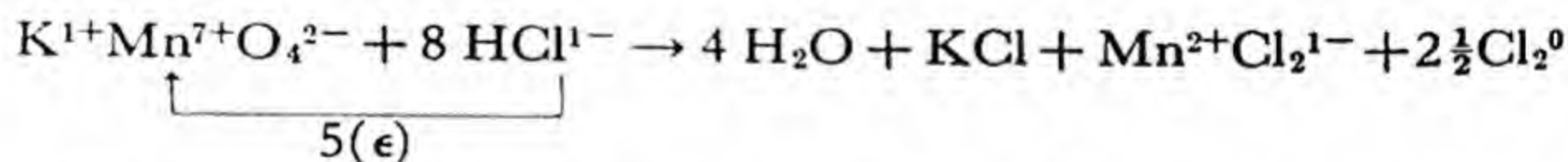


Fig. 74. Preparation of chlorine.

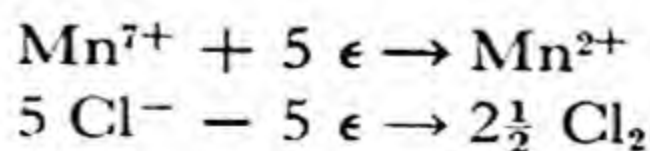
Without delay we set down enough HCl to convert all the oxygen into water:



The drop in positive valence number of the manganese from 7 to 2 requires a donation of 5 electrons from the negative chlorine in HCl. Three chlorine atoms reappear in combined form in KCl and MnCl_2 . To avoid the $2\frac{1}{2} \text{Cl}_2$ we double all items in the last trial equation, securing:



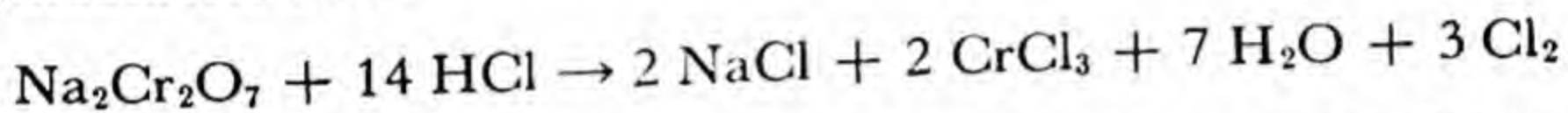
The half reactions are:



In only ten of the HCl molecules has the valence number of the chlorine changed. The chlorine in the other six molecules reappears in the chlorides of manganese and potassium with no valence change.

To a question as to how we know that the products of this reaction are KCl and MnCl₂ it may be answered that analysis of the final solution gives the information. At this early stage we are obliged to give the student the correct formulas for the products. Potassium permanganate, being soluble in water, is in better contact with the acid than is the insoluble manganese dioxide.

Sodium dichromate is also efficient in oxidizing concentrated hydrochloric acid:



3. Compare this equation with the one for potassium permanganate. Balance it electronically. The chromium valence number in Na₂Cr₂O₇ is six.
4. How many liters of chlorine may be released by the action of 32 g. of potassium permanganate on hydrochloric acid?

In balancing the equations representing the action of most of the oxidizing agents on HCl it is helpful to remember that the hydrogen of the HCl unites with all the oxygen of the oxidizing agent to form water while the metal (or metals, as in KMnO₄) unite with all the chlorine they can hold (forming KCl, MnCl₂, etc.). The rest of the chlorine, if there is any, is liberated. Similar statements apply to HBr and HI.

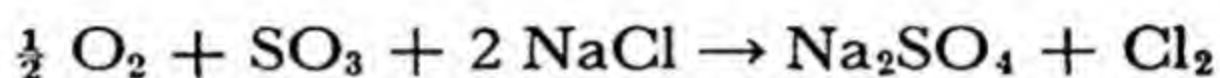
Chlorine by Electrolysis. The leading commercial method of making chlorine is the electrolysis of water solutions of sodium chloride. Chlorine is evolved at the anode, which must be made of carbon, usually in the form of graphite, because the gas is so active it would react with metal anodes. At the cathode, usually iron, sodium hydroxide, and hydrogen are the products. Since chlorine in the presence of water reacts with sodium hydroxide, it is necessary to keep the solutions around the two electrodes from mixing.

In any electrolytic cell the current enters at the positive anode and leaves at the negative cathode.

Not long ago electrolytic sodium hydroxide was in much greater demand than the accompanying chlorine. Now greatly increased amounts of chlorine are wanted. In the United States over 1,800,000 tons of chlorine were used in 1948.

Molten sodium chloride conducts electricity and can thus be decomposed into chlorine and sodium. With no water present the sodium accumulates. This is one of the commercial sources of metallic sodium although in actual practice some sodium carbonate (Na_2CO_3) is added to lower the melting point of sodium chloride.

A recent development in chlorine manufacture is the reaction between hot, dry sodium chloride and sulfur trioxide.



Physical Properties. Chlorine is a greenish-yellow gas 2.49 times as heavy as air. One liter weighs 3.214 g. under standard conditions. One hundred volumes of water dissolve 226 volumes of chlorine. It can be liquefied at 18° by 16.5 atmospheres pressure and its critical temperature is 146° . The liquid boils at -33.6° and freezes at -102° . When collected over water there is some loss because it dissolves in and reacts with water. It is less soluble, however, in water saturated with common salt. Since it attacks mercury it may not be collected over that liquid. Usually it is led into the bottom of any vessel filled with air and, being 2.49 times as heavy, displaces the air upward. Water saturated with chlorine at 0° deposits crystals of $\text{Cl}_2 \cdot 8 \text{H}_2\text{O}$. These have a very high vapor tension, decomposing readily on being warmed slightly.

Chlorine, under pressure, is now shipped in tank cars containing 15 tons of the liquid element. Dry chlorine does not attack steel.

Chemical Properties. Chlorine is one of the most active elements, more active than oxygen. It unites with nearly all the elements to form *chlorides*. It is fatal to breathe air containing 1 part of chlorine in 1000.

1. Action on Elements. The metals, with but few exceptions, unite with chlorine. A piece of sodium in a bottle of *dry* chlorine

gradually becomes sodium chloride, but if the sodium is first heated it burns brilliantly in the chlorine. So does calcium, forming calcium chloride. Thin copper foil, if heated, seems to burst into flame in a jar of chlorine.

For a lecture-table experiment it is most convenient to evacuate a flask containing crumpled copper leaf (Dutch metal), close the stopcock, connect with a flask of chlorine (Fig. 75), and then open the stopcock. As the chlorine rushes up the *wide* tube into the upper flask a flash of something resembling flame appears.

Even platinum is attacked by the gas. Most of the non-metals are attacked. Sulfur burns in chlorine to form sulfur chloride, S_2Cl_2 , used in the manufacture of mustard gas and, to some extent, in rubber curing.

Phosphorus unites with chlorine (burns in it in fact) to form a colorless liquid (PCl_3), phosphorus trichloride. With an excess of chlorine this becomes PCl_5 , phosphorus pentachloride, a yellow solid.

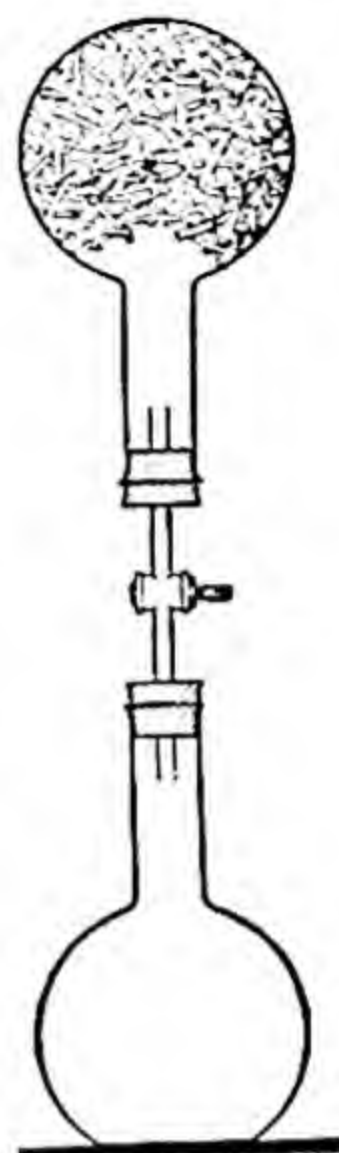


Fig. 75. Chlorine reacts with copper foil.

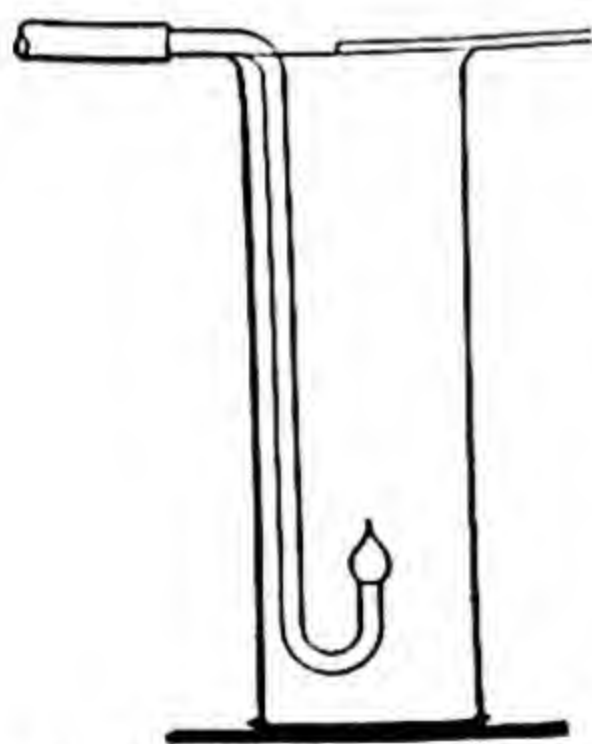
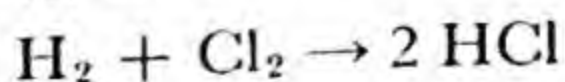


Fig. 76. Burning methane in chlorine.

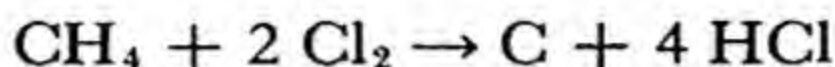
Chlorine and hydrogen unite very slowly in the dark, rapidly in diffused light, and explosively in bright sunlight or the light of burning magnesium. Hydrogen chloride is formed. If a jet of burning hydrogen is lowered into a bottle of chlorine, it continues to burn with evolution of light and heat and formation of hydrogen chloride (Fig. 76). Direct union of the two gases is being used to some extent now to form pure "synthetic hydrochloric acid." There is, therefore, such a thing as combustion without oxygen:



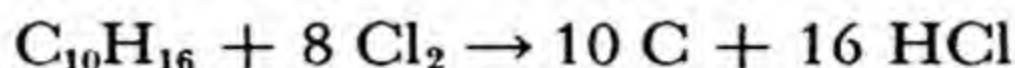
2. Action on Compounds. Chlorine will pull the hydrogen out of compounds and form hydrogen chloride. Natural gas (largely

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CH₄, methane) will burn in chlorine just as well as does hydrogen, but the flame is smoky, due to the liberated carbon (Fig. 76).

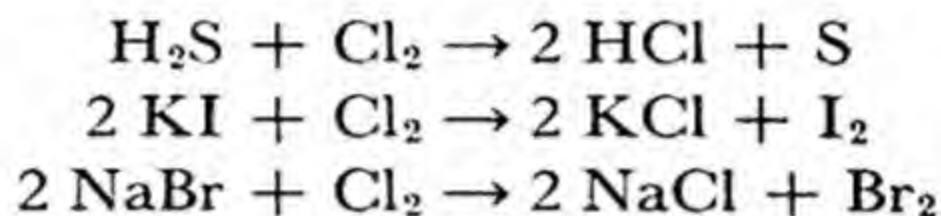


A burning candle lowered into a jar of chlorine burns with a smoky flame. A paper wet with warm *turpentine*. C₁₀H₁₆, bursts into smoky flame in chlorine. The reaction is similar:

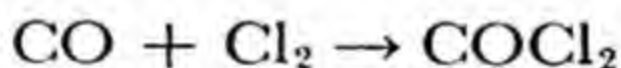


5. How many liters of hydrogen chloride at 0° and 760 mm. can be formed by the action of chlorine on 175 g. of turpentine? Solve two ways.

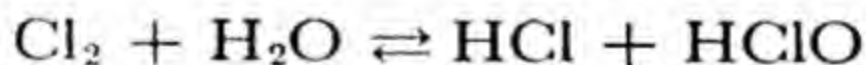
Chlorine also displaces some elements from compounds:



Here, sulfur, iodine, and bromine are displaced. Chlorine is a more active element than these three. With carbon monoxide, catalyzed by charcoal, at 100°, it unites to form phosgene, one of the most effective poison war gases:

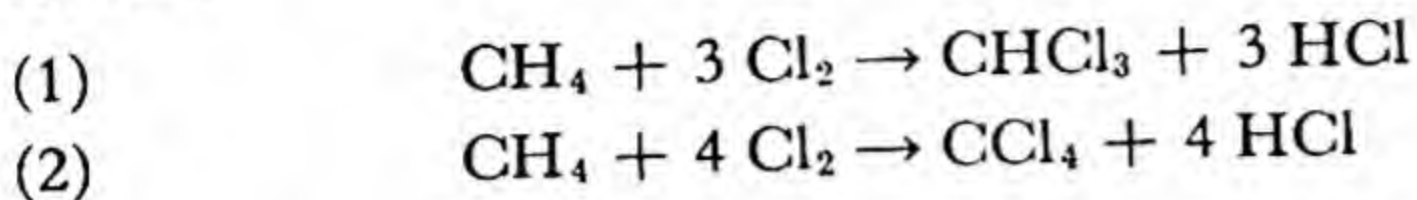


Chlorine not only dissolves in cold water (6.3 g. per liter) but reacts with it:



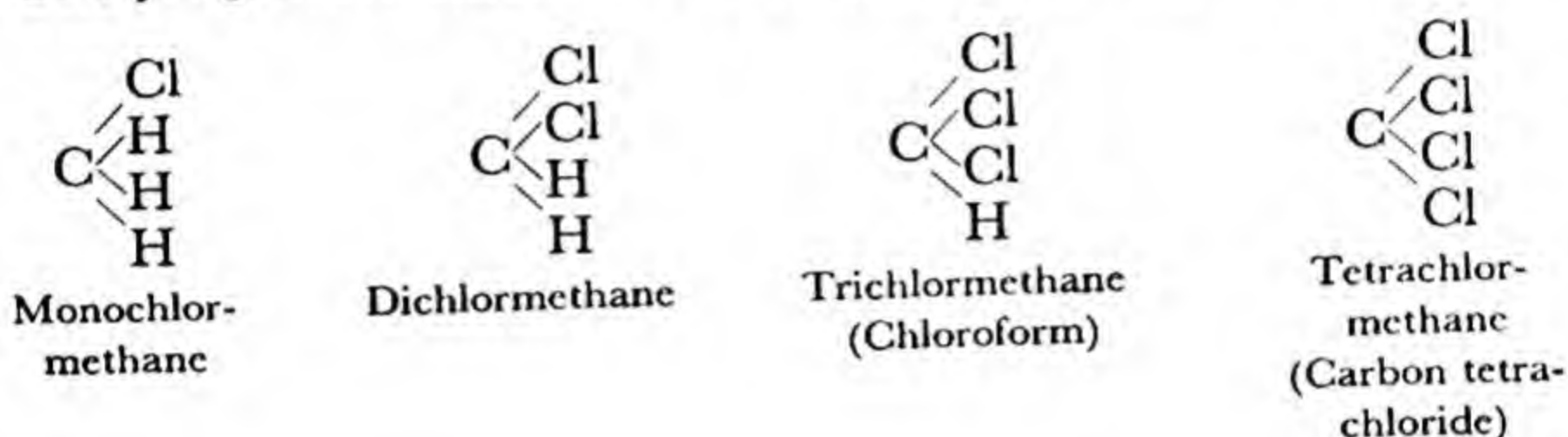
This is a reversible reaction, but the hypochlorous acid (HClO) slowly decomposes into hydrochloric acid and oxygen. Since this decomposition is accelerated by sunlight, chlorine water is best kept in dark bottles. Finally the equilibrium is displaced completely to the right and there is no longer any dissolved chlorine left, merely a solution of hydrochloric acid. The equilibrium is disturbed to the right rapidly if there is some reducing agent present to take up the oxygen from the hypochlorous acid. In other words the instability of hypochlorous acid makes it a good oxidizing agent.

We referred previously to the burning of a jet of methane (CH_4) in chlorine. In the sunlight the two gases react slowly as follows:



CHCl_3 is chloroform and CCl_4 is carbon tetrachloride. This kind of displacement is sometimes called *substitution*. The hydrogen displaced is not set free but unites with part of the chlorine.

The progressive chlorination is represented graphically below:

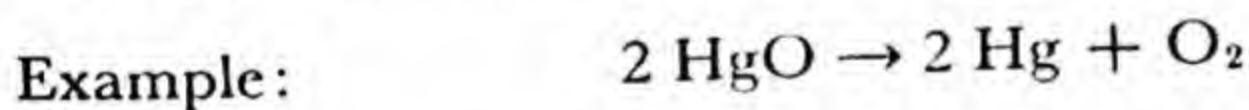


Types of Chemical Reaction.

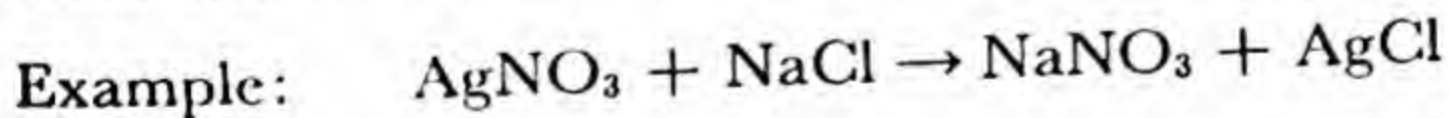
1. *Combination*. Two substances unite to form one substance.



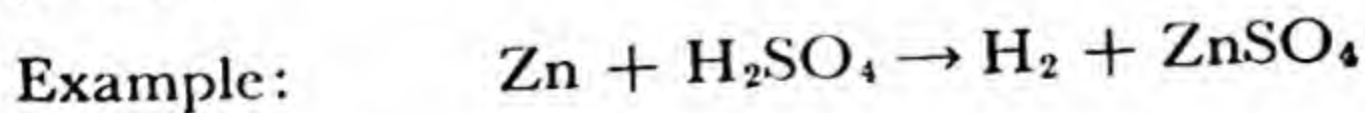
2. *Decomposition*. One substance decomposes into two or more.



3. *Double Decomposition*. Two substances react to form two other substances.



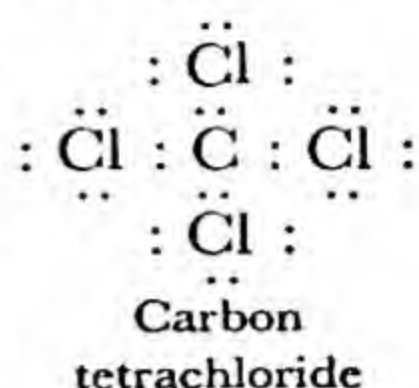
4. *Displacement*. One element displaces another from a compound.



5. *Substitution*. See above.

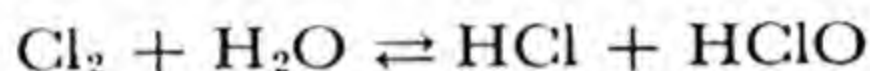
6. Write three examples of each type.

Carbon has 4 valence electrons; chlorine has 7. In the graphic formula on the right each chlorine atom is sharing (covalence) one electron with carbon, which reciprocates. Consequently a complete outer shell of eight electrons is built up for all the atoms concerned.



Uses of Chlorine. Chlorine in normal times finds its greatest use in preparing chlorine derivatives of the hydrocarbons and other organic compounds. The second use is as a bleaching agent, especially for paper and textiles. Colored strips of calico, red geraniums, etc., hung in bottles of chlorine soon lose their color. If, however, the gas and the colored object are thoroughly dried, no bleaching takes place.

The effect of water is easily understood from the equation just given:



The hypochlorous acid oxidizes colored substances into colorless ones, therefore the chlorine bleaches indirectly. Printer's ink cannot be bleached because its color is due to carbon, on which hypochlorous acid has no effect. Chlorine is too destructive to be used on silk, feathers, and the more delicate materials. Even cotton is slightly weakened, so the chlorine must be thoroughly washed out. Great quantities of the gas are passed over lime to form bleaching powder, from which chlorine can be released as needed.

Many great cities (85 per cent of them) add a little chlorine to their water supplies to kill bacteria, which it does most efficiently and cheaply (see page 123).

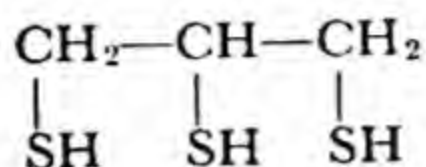
Production of chlorine in the United States has risen rapidly in recent years to an annual total of 1,800,000 tons.

Gold may be extracted from its ores by the action of chlorine on them to form soluble gold chloride. This is only one of the processes used.

Chlorine is essential to most of the poison gases used in modern warfare. Rolling clouds of chlorine were used in the first gas attacks. Mustard gas ($\text{C}_2\text{H}_4\text{Cl}_2\text{S}$), phosgene, COCl_2 , chlorpicrin (CCl_3NO_2), — these demand huge quantities of chlorine. Mustard gas (dichlorodiethylsulfide) is still the most

effective toxic gas, partly because of the ease and safety of its manufacture which is essentially the reaction between ethylene (C_2H_4) and sulfur monochloride (S_2Cl_2). The raw materials are easily prepared in quantity. Lewisite is $ClCH=CHAsCl_2$, and the newer nitrogen mustards, $(ClCH_2\cdot CH_2)_3N$.

As a good result of war gas research the British developed "BAL" with formula

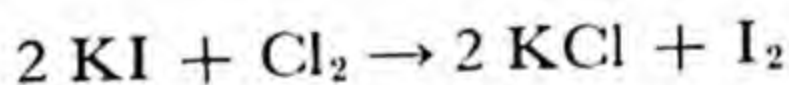


to counteract Lewisite gas. It was found to have great value in medicine.

One of the best tear gases (so useful to the police) is benzyl bromide, $C_6H_5CH_2Br$.

Uses of chlorine	{	Chlorinated hydrocarbons (solvents and degreasers, etc.)
		Bleaching paper and cotton
		Ethylene glycol (anti-freeze)
		Water purification
		Neoprene rubber
		Some plastics
		Gold extraction

Tests. Minute traces of chlorine are readily detected by smell. A filter paper soaked in a solution of potassium iodide and starch turns blue in the gas. Chlorine sets the iodine free, thus:



The *free* iodine then reacts with the starch with the development of a blue color.

BROMINE

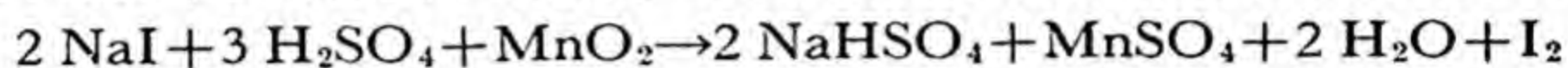
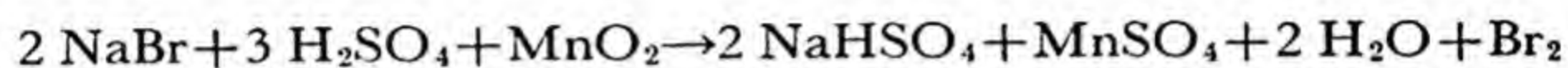
History. Balard, in 1826, released bromine from a salt liquor by the action of free chlorine. This is the most modern method of commercial preparation we have today, a century later. He also treated a salt, which he later found to be potassium bromide, with concentrated sulfuric acid and manganese dioxide and obtained bromine. Even this method is still in use.

Occurrence. *Bromine* (Br) in the form of magnesium bromide ($MgBr_2$) and sodium bromide ($NaBr$) is far less abundant than the chlorides, but it is found with sodium chloride in sea water, in the great salt layers at Stassfurt, Germany, and in the salt brines

of Michigan and West Virginia. The Dead Sea contains much magnesium bromide. One cubic mile of sea water contains 310,000 tons of combined bromine.

Preparation. Oxidation of the simple halogen acids serves well in the preparation of bromine, chlorine, and iodine.

A mixture of sodium bromide, manganese dioxide, and concentrated sulfuric acid is heated moderately. The vapors of bromine are condensed in a cooled flask (Fig. 77). Similar reactions are given in steps on pages 172 and 173.



In other words, the oxidation of hydrogen bromide ($2 \text{HBr} + \text{O} \rightarrow \text{H}_2\text{O} + \text{Br}_2$) is a part of the mechanism of the reaction.

The brine pumped up from the salt beds underlying Midland, Michigan, and vicinity contains 0.14 of one per cent bromine (as

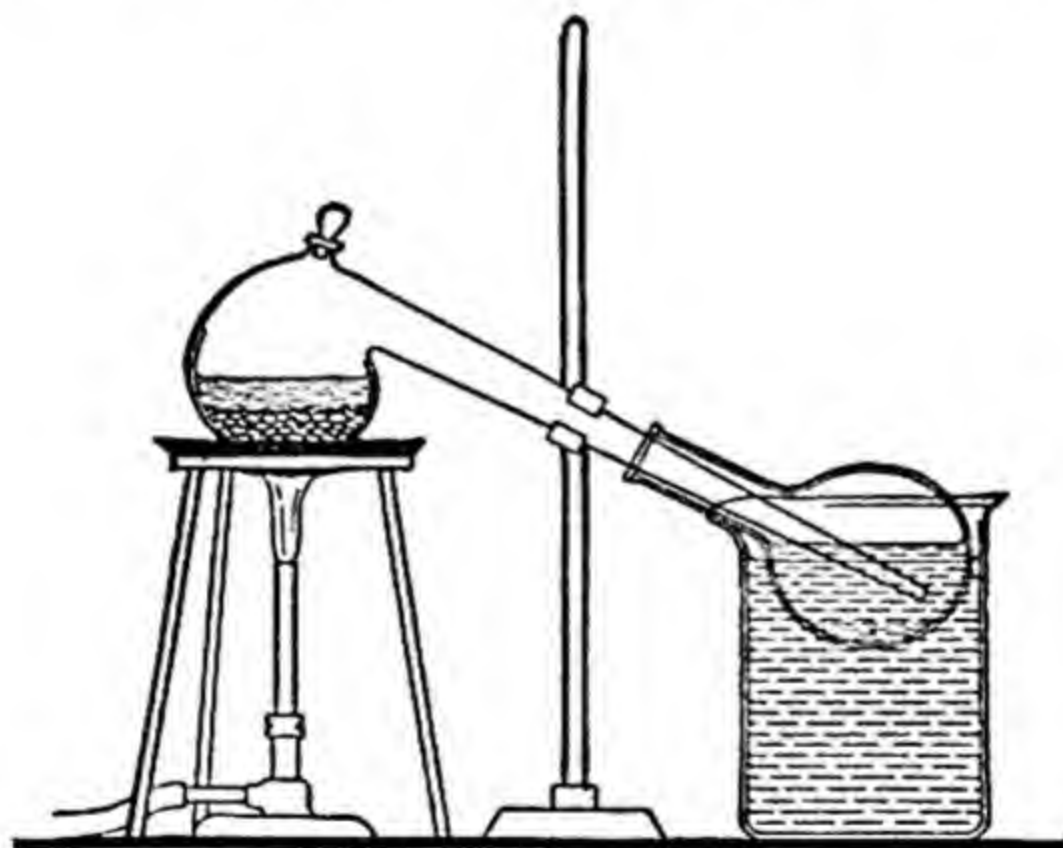


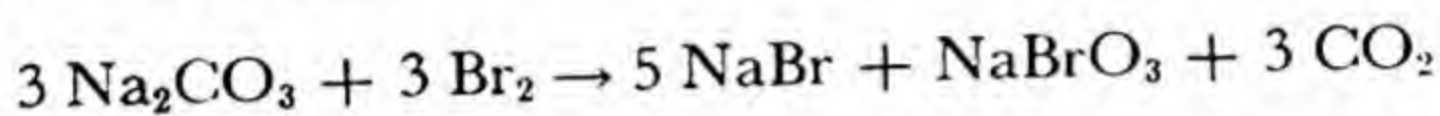
Fig. 77. Preparation of bromine by heating a mixture of potassium bromide, manganese dioxide, and concentrated sulfuric acid.

sodium and magnesium bromides). After concentrating to crystallize out most of the salt the remaining "bitter liquor" is electrolyzed at a voltage high enough to release all the bromine but too low to discharge any chlorine.

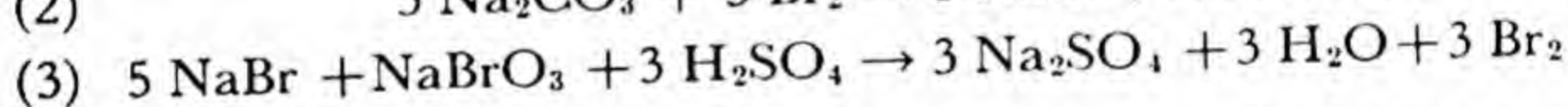
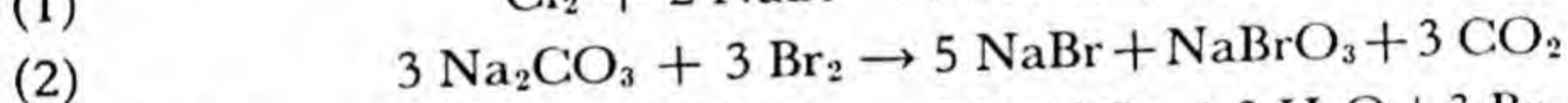
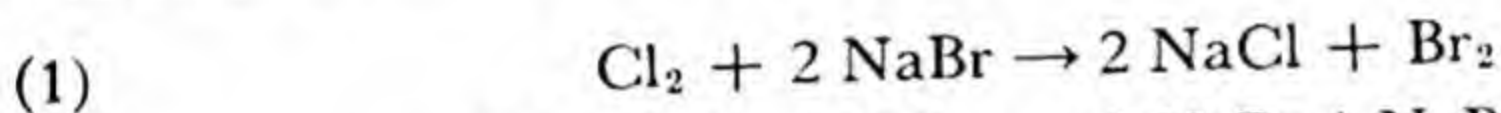
A stream of warm air carries off the bromine. Some of the bromine is cooled and condensed as a liquid, but most of it is

led up through a splash tower against a "counter current" of sodium carbonate solution. Sodium hydroxide could be used but costs more. The reactions are represented by equations (1) and (2) below.

No bromine escapes, for it meets at the top a stream of fresh sodium carbonate solution. No sodium carbonate gets through, for it meets a stream of fresh bromine vapor at the bottom. Proper adjustment of the two opposing streams gives efficiency. Increasing either stream after adjustment would mean a loss of bromine or of sodium carbonate as the case might be.



Bromine is also obtained from sea water when it is acidified and treated with chlorine. The bromine liberated is blown out with air and caught in a spray of sodium carbonate solution which is later boiled to a dry mixture of the bromide and bromate that is convenient for transportation. Equation (3) below explains the release of bromine when desired by the purchaser.



Here the sulfuric acid liberates HBrO_3 (bromic acid) which oxidizes the HBr also liberated.

The ocean is a limitless source of bromine with 310,000 tons of combined bromine in each cubic mile.

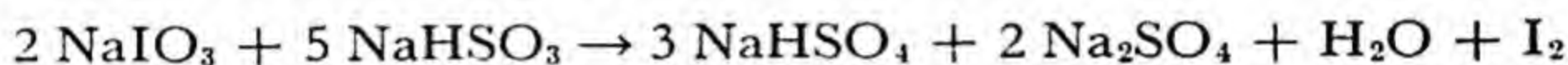
Uses. Bromine is used in making some aniline dyes, and in making potassium bromide (a valuable nerve sedative). Silver bromide is the sensitive material on photographic plates.

In 1924 tetraethyl lead came into extensive use as an "anti-knock" addition to gasoline. About 2 ml. of ethylene bromide, $\text{C}_2\text{H}_4\text{Br}_2$, per gallon of gasoline are required to furnish enough bromine to change the lead set free in the explosion into PbBr_2 . Free lead would injure the ignition points. This development has forced the United States to increase bromine production to more than 40,000 tons annually.

History. Soon after Davy proved that chlorine is an element iodine was prepared by Courtois, who heated the ash of seaweed with concentrated sulfuric acid and obtained violet vapors. This method, with some modification, is still used. Courtois did not know what he had made, but in 1814 Gay-Lussac proved that the new substance was an element and gave it the name "iodine," from the Greek for "violet."

Preparation. Nearly all our iodine is obtained from the beds of Chile saltpeter (NaNO_3), where it is found to the extent of 0.2 per cent as sodium iodate (NaIO_3).

The sodium iodate is decomposed by sodium bisulfite:



7. Would iodine displace bromine from a bromide?

Chile produces annually almost 800 tons of iodine and could easily produce ten times as much. This monopoly has led to prices beyond reason. Our annual needs total over 2,000,000 pounds, and most of it is imported. In the past several years iodine has been extracted from the salt brine of some oil wells in California and Louisiana, cutting to nearly one-third the price of \$4.00 per pound set by the Chilean monopoly. New uses for iodine are sought. Have you suggestions?

Properties. All the halogens unite directly with phosphorus. Iodine and white phosphorus unite vigorously with the evolution of heat, and burst into flame. Several inter-halogen compounds such as ICl and IF_5 are known but they are not very stable.

Iodine dissolves in many organic liquids, such as chloroform, carbon disulfide, hydrocarbons (in all these with violet color), alcohol, and ether (in these two with brown color). Although only slightly soluble in water, it dissolves readily in an aqueous solution of sodium or potassium iodide:



The potassium triiodide (KI_3) is a rich red in color and very soluble, but all efforts to separate it from solution fail.

Crystals of iodine in the open air volatilize. On heating cautiously, iodine changes rapidly into violet vapors without passing through the liquid stage (but it can be melted). Such a change is called *sublimation*. Iodine is sublimed to separate it from impurities.

Uses. Iodine finds application as silver iodide in photography, as iodides in medicine, and in the manufacture of some dyes. Iodoform (CHI_3) is a valuable antiseptic. Tincture of iodine, about a 3 per cent alcoholic solution of the element with some KI, is of great service in medicine as an antiseptic. As a laboratory reagent in quantitative analysis iodine is well known.

A small amount of an organic iodine compound, thyroxin, is found in the thyroid gland of man. Where we are deficient in this, goiter or cretinism develops. In certain areas the original iodides have been leached out of the soil — and goiter is prevalent. Much “iodized salt” is sold in grocery stores (0.01 per cent NaI). It is also added to cattle feed.

FLUORINE

History and Preparation. As early as 1670 chemists knew that the mineral fluorspar (CaF_2), when warmed with concentrated sulfuric acid, produced a gas that attacked glass. Not until 1807 was the acid (HF in aqueous solution) prepared by Gay-Lussac. All efforts to release the element fluorine from this acid failed, due to the great activity of fluorine, until Moissan in 1886 isolated it by electrolyzing a solution of potassium hydrogen fluoride in liquid hydrogen fluoride contained in a cooled platinum U-tube. Today such electrolysis is carried out in steel vessels using graphite anodes and steel cathodes. The liquid is fused $\text{KF} \cdot 2 \text{HF}$.

A variety of fluorine compounds (both from fluorine and hydrofluoric acid) are available, some in commercial quantities and others only for experimental purposes. One important compound commercially available is sulfur hexafluoride. This inert gas has a greater dielectric strength than any other known gas. For this reason it is a most promising gaseous insulating medium for high voltage applications.

Occurrence. *Fluorine* (F) is found as fluorspar (CaF_2), cryolite (Na_3AlF_6), and apatite ($\text{CaF}_2 \cdot 3 \text{Ca}_3(\text{PO}_4)_2$). Cryolite occurs in Greenland and is of great importance in the production of the metal aluminum.

Properties. Fluorine, because of its great reactivity, is difficult to prepare and to keep.

It has been observed that many children in western areas, wherever drinking water contains over two parts fluorine per million, develop mottled teeth. Methods of removing fluorine from water have been devised, such as treatment with tricalcium phosphate or bone ash. And yet a trace of fluorides seems to build up resistance to decay in teeth.

A few cities are now putting one part per million of fluorine (as sodium fluoride) in their water supplies to lessen decay of teeth. Three times this much might cause mottled teeth. The experiments are being watched with interest.

A hot glass rod will burn in an atmosphere of fluorine, forming fluorides, not oxides. Cotton, immersed in liquid fluorine, explodes violently.

The fact that fluorine is the most active element makes its compounds exceptionally stable. This stability of organic compounds is now receiving great attention from industry and a rapid development in this field seems certain.

Uses of Fluorine Compounds. Ammonium fluoride is a disinfectant for brewery vessels. Sodium fluoride is an effective wood preservative and insecticide. Sodium hydrogen fluoride is much used in polishing granite. Magnesium silicofluoride (MgSiF_6) is soluble and finds use in hardening concrete. The mineral fluorspar, CaF_2 , is essential as a flux in making open-hearth steel and is used in making white opaque glass and enamels. Melted fluorides are used in the electrolytic manufacture of aluminum and, possibly, of magnesium. A fluorocarbon plastic is highly resistant to chemical attack.

Hydrofluoric acid and its acid salts are used in etching glass (electric light bulbs, apparatus, etc.); the gas hydrogen fluoride is used as a catalyst in the petroleum industry; and the acid in preparing fluorides.

Antimony trifluoride, SbF_3 , is an important catalyst for a number of organic reactions and is used in making "Freon," CF_2Cl_2 , the non-toxic, non-inflammable liquid used in the refrigerators of many households and all submarines. Freon (liquid, under pressure) is the solvent for pyrethrum used by the Army and Navy in warfare on mosquitoes. The finely-divided spray or mist formed when pressure is released in such a "bomb" is extremely effective.

The Halogens Compared. Iodine is a solid at room temperatures, bromine a liquid, and chlorine and fluorine are gases. At 0° chlorine dissolves in 100 ml. of water to the extent of 1.49 g., bromine 4.3 g., and iodine 0.32 g. Fluorine reacts rapidly and completely with water to form hydrogen fluoride and oxygen.

Exercises

8. Calculate the weight of chlorine obtained by complete interaction of (a) manganese dioxide, (b) potassium permanganate, on 200 g. of sodium chloride in the presence of an excess of sulfuric acid.
9. How much potassium bromide (95 per cent pure) is necessary for the preparation of 150 g. of bromine?
10. What volume of bromine vapor at 100°C . and 760 mm. can be produced from 24 ml. of liquid bromine? The density of liquid bromine is 3.12 g. per ml. at 20° .
11. What volume of chlorine at 10° and 750 mm. will be required to displace all the bromine from 618 ml. of a 0.5 normal solution of sodium bromide?
12. How could you extract free iodine from a salt brine containing a very low concentration of sodium iodide?
13. Must the iodide ion be oxidized or reduced to convert it into free iodine? Explain.
14. What is the chief use of bromine?
15. List the halogens in order of decreasing tendency to take up (gain or "steal") electrons from some outside source; i.e., put first the halogen that gains an electron most readily and last the one that gains an electron least readily.
16. Give an illustration of "counter current" reactions.

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188 CHLORINE, BROMINE, IODINE, AND FLUORINE

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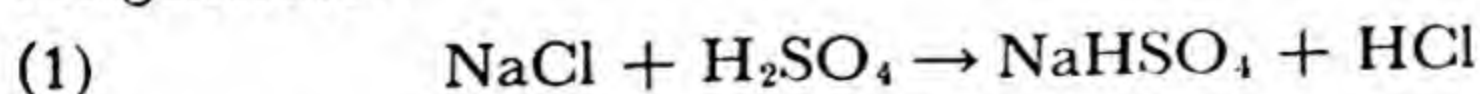
Chapter 17 THE SIMPLE HALOGEN ACIDS

HYDROGEN CHLORIDE

Priestley first made the anhydrous gas, hydrogen chloride, in 1772. Its water solution was called "muriatic" acid and is still so referred to commercially. Very few uses for the acid were developed until it became cheap as a by-product of the Le Blanc soda process. A little hydrochloric acid is found in the gastric juice of the stomach where it serves as an activator of pepsin.

The most used laboratory and commercial method of preparation is the treatment of any suitable chloride (sodium chloride is the cheapest) with concentrated sulfuric acid. In practice there is less frothing if the acid is slightly diluted. As shown in Fig. 78 the delivery tube should barely touch the surface of the water.

The gas is so soluble that otherwise water might rush back into the generator.



If an excess of salt is used and the temperature raised, the reaction is somewhat different:

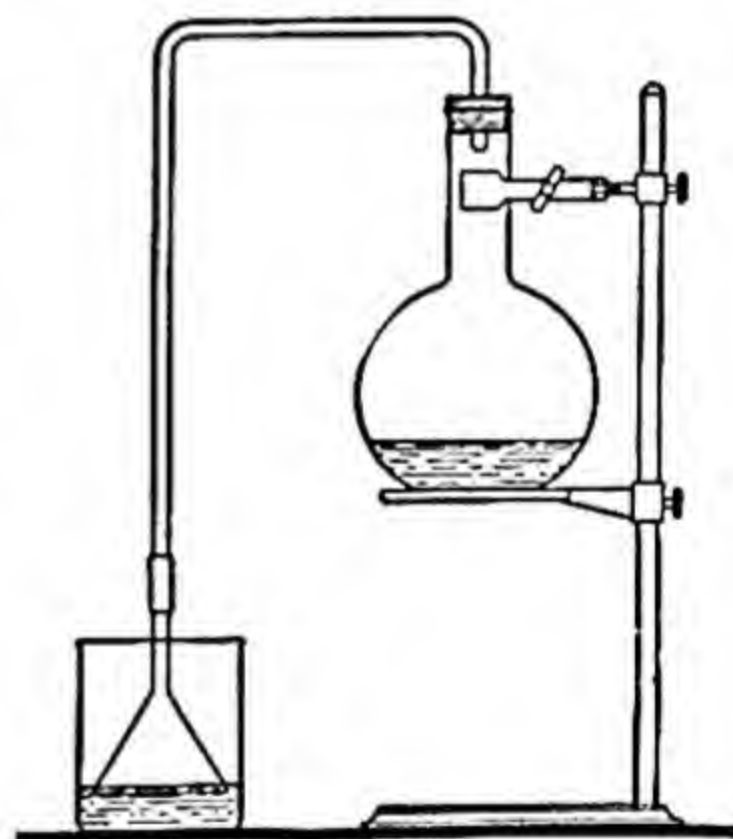
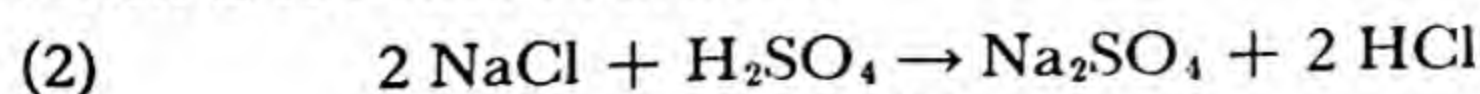
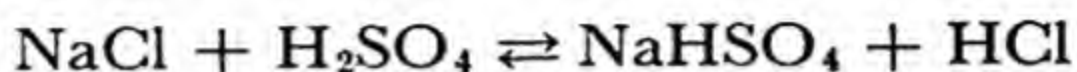


Fig. 78. Preparation of hydrochloric acid.

In (1) sodium hydrogen sulfate is formed and in (2) sodium sulfate. The hydrogen chloride escapes as a gas because it is insoluble in the concentrated sulfuric acid.

The conditions of (1) are radically changed when dilute sulfuric acid is used:

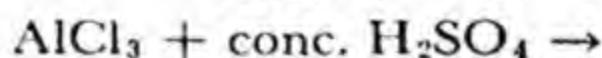
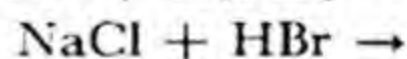
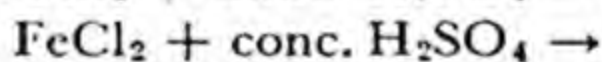
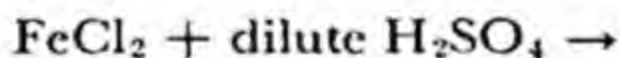


The reaction is reversible because there is sufficient water to dissolve the hydrogen chloride. Since it is then in good contact with the sodium hydrogen sulfate, there is nothing to hinder reaction to the left. No gas escapes. This is an impossible method for securing the evolution of hydrogen chloride.

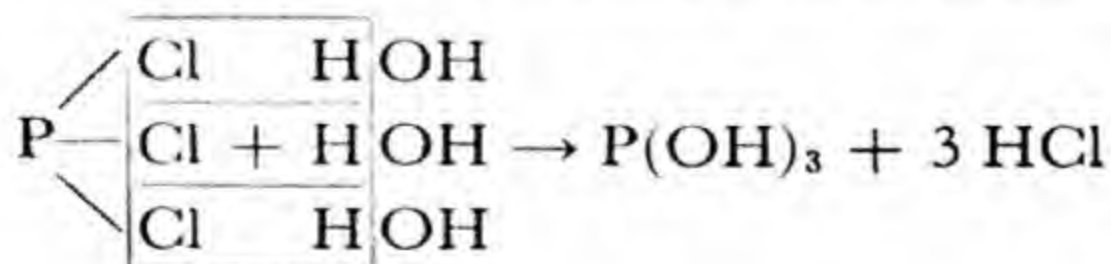
Any soluble metallic chloride serves as a source of hydrogen chloride. The acid used with the metallic chloride must not react with the desired hydrogen chloride as would nitric or any other oxidizing acid. Phosphoric might seem as good as sulfuric acid, since it also has a higher boiling point than most acids, but unfortunately it reacts too slowly. Sulfuric acid is always used because it is cheap, is less volatile than hydrogen chloride (or most acids, in fact), and does not react with hydrogen chloride.

Exercise

1. Complete:



The chlorides of some non-metals react with water to form hydrogen chloride. This is an example of hydrolysis:



The simplest method, in principle (although not in practice), to make hydrogen chloride is the burning of chlorine in an atmosphere of hydrogen. Combustion takes place as truly as in the

oxyhydrogen blowpipe. Much pure hydrochloric acid is now made commercially by this method in order to utilize the hydrogen escaping as a by-product in the electrolytic manufacture of chlorine and sodium hydroxide from NaCl.

Great quantities of hydrogen chloride are formed as by-products of the chlorination of hydrocarbons.

Thin-walled tubes of tantalum are coming into use as containers for the absorption of hot HCl gas in water to yield high-strength acid. Tantalum has great resistance to acid corrosion, a high melting point, and a high rate of heat transfer (important in cooling the hot acid).

Physical Properties. Hydrogen chloride is a colorless gas with a choking odor, and is enormously soluble in water. If the upper flask in Fig. 79 is filled with hydrogen chloride gas, the introduction of a very little water from below creates a partial vacuum. The gas dissolves quickly in the water and more water rushes in. One volume of water dissolves 455 volumes of the gas at 15° and 760 mm. The solution is called hydrochloric acid. The gas "fumes" in moist air by condensing the invisible moisture into visible droplets of solution. The gas is somewhat heavier than air; one liter weighs 1.642 g. at standard conditions. At 0° it is liquefied by 28 atmospheres' pressure, but at -84° C. one atmosphere liquefies it. This is, then, its boiling point. It freezes at -112.5° C. and its critical temperature is 52° C.

When a concentrated solution of hydrochloric acid is heated it loses hydrogen chloride more rapidly than water until the concentration falls to 20.24 per cent at 760 mm. pressure. Then the rest of the liquid distills unchanged at 108.58° . This product is called the acid of *constant boiling point*. If very dilute hydrochloric acid is boiled, steam passes off more rapidly than hydrogen chloride, until the concentration rises to 20.24 per cent. This does not indicate the

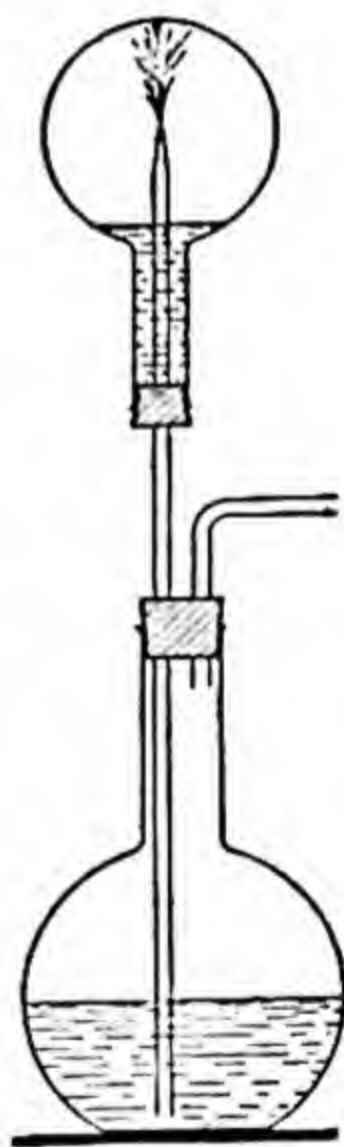


Fig. 79. Hydrogen chloride fountain.

existence of a compound of hydrogen chloride and water, for by merely changing the pressure the composition of the distillate changes.

The concentrated "chemically pure" acid of commerce has a specific gravity of 1.2 and contains 37 per cent hydrogen chloride and 63 per cent water by weight.

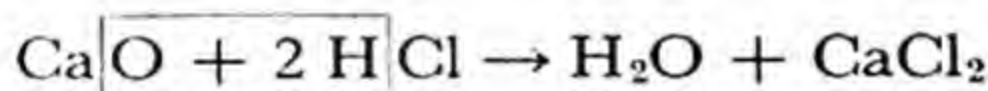
2. How many grams of the gas in 850 ml. of "C. P." hydrochloric acid?

Chemical Properties. As a dry gas hydrogen chloride is not very active, but in water solution it ranks as one of the "strongest" acids. Like all acids, its solution is sour and turns blue litmus paper red.

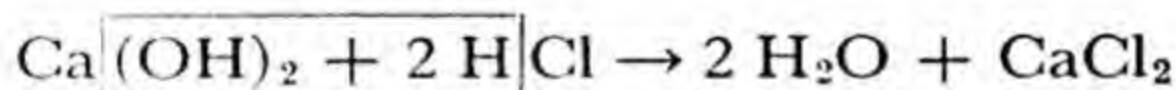
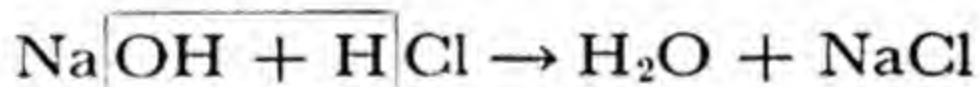
The metals more active than copper displace hydrogen from hydrochloric acid:



Oxides of the metals react with it to form water and a chloride of the metal:

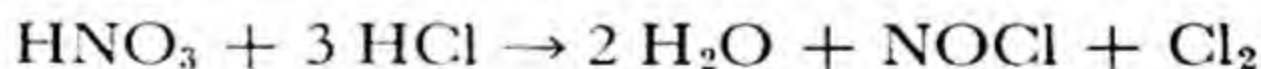


Hydroxides of the metals (bases) react with hydrochloric acid to form water and metallic chlorides:



The base and acid can be mixed in such proportions that the solution is no longer sour or soapy, nor does it affect litmus. We say the acid has *neutralized* the base and vice versa.

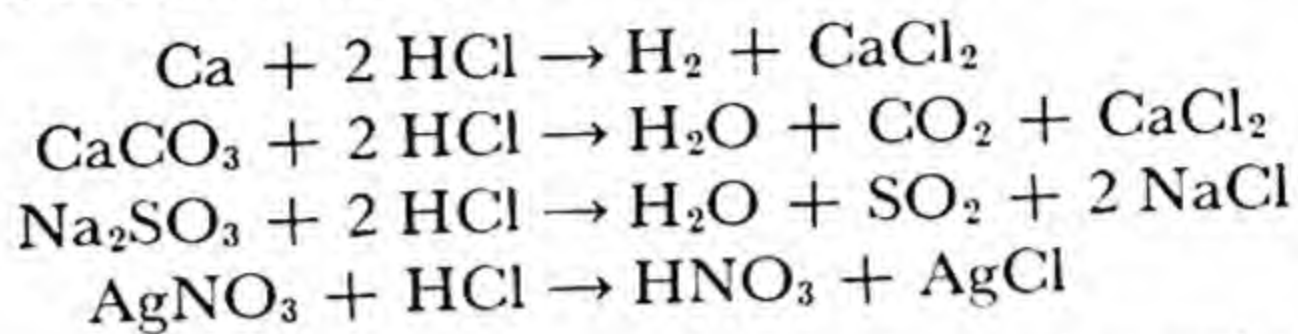
Nitric acid oxidizes hydrogen chloride into water and chlorine. Another product, nitrosyl chloride, NOCl, is also formed:



A mixture of three volumes of concentrated hydrochloric acid and one volume of concentrated nitric acid is called *aqua regia* because it dissolves gold.

That hydrogen chloride is a reducing agent is shown by the fact that it can be oxidized.

Uses. Hydrochloric acid is used to form many chlorides. Many metals, all metallic oxides and hydroxides, and some salts react with it to form chlorides. Carbonates and sulfites of the metals (see below) all react with hydrochloric acid to form chlorides:



In the fourth reaction the silver chloride formed is only slightly soluble and therefore precipitates when formed in a solution. It is one of the three metal chlorides insoluble in water, the other two being mercurous chloride and lead chloride. This is worth remembering.

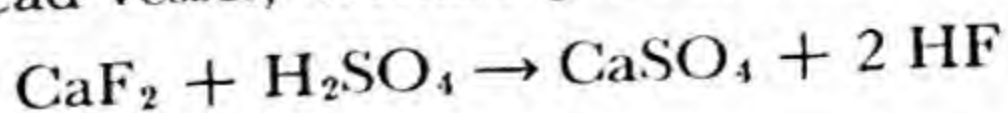
Hydrochloric acid is used, also, to clean metals (reacting with the oxides). For all purposes we use 400,000 tons yearly, calculated as 100 per cent. A recent application is found in the acid method of opening up oil-bearing limestone strata.

Hydrogen chloride reacts with rubber to form "chlorinated rubber." This can be worked into flexible, transparent films and sheeting that are very useful in preserving fresh fruits for shipment.

Test. A solution that turns blue litmus red and forms a white precipitate of silver chloride when silver nitrate is added indicates the presence of hydrogen chloride. As a gas it can be detected by holding in the gas a drop of silver nitrate solution on a glass rod. A milkiness in the drop is a positive test, confirmed by the reddening of moist blue litmus paper.

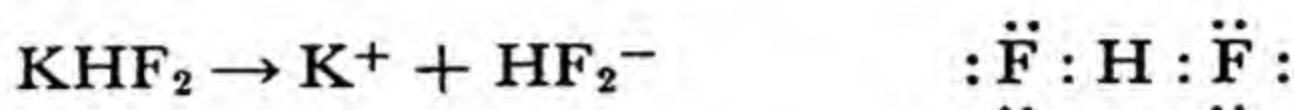
HYDROGEN BROMIDE, HYDROGEN IODIDE, AND HYDROGEN FLUORIDE

The Simple Halogen Acids. HF, HBr, and HI resemble HCl in many respects. All are colorless gases, irritating in odor, that are extremely soluble in water, form acid solutions, and fume in moist air. They all may be made by direct union of the elements, but with certain differences. In practice hydrogen fluoride is made by warming concentrated sulfuric acid and calcium fluoride in a lead vessel, because glass is attacked:

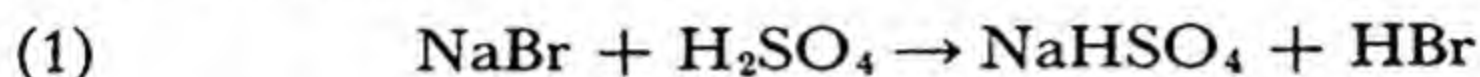


The simple formula, HF, represents hydrogen fluoride above 90° as a gas or in dilute solution. In liquid form H_2F_2 and higher polymers are present.

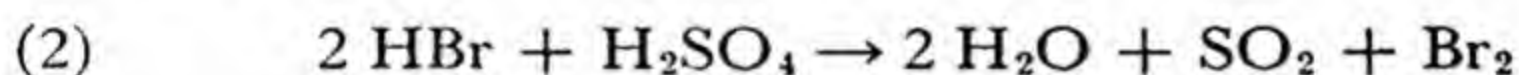
In the complex anion, HF_2^- , from KHF_2 , the hydrogen atom probably acts as a "hydrogen bond," to hold the two fluorine atoms together.



We might reasonably expect hydrogen bromide to be produced by the treatment of a bromide with concentrated sulfuric acid:

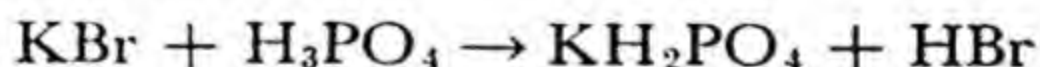


Yet when we do this we observe a red-brown gas in addition to the colorless, fuming hydrogen bromide. A paper wet with starch and potassium iodide solutions turns blue and from this and the color and the peculiar, irritating odor we decide that bromine was released. The hydrogen bromide is evidently oxidized by the concentrated sulfuric acid. When rather dilute sulfuric acid is used, no colored gas escapes and no color appears. The reaction is reversible (as with chlorides) because of the great solubility in water of hydrogen bromide. But it is noteworthy that no red-brown color can be seen — dilute sulfuric acid is not an oxidizing agent. With concentrated acid equation (1) is followed by (2):



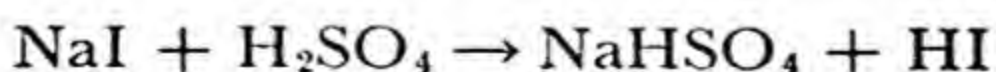
Each molecule of hot, concentrated H_2SO_4 loses one oxygen atom to the hydrogen of the hydrogen bromide and leaves H_2SO_3 , which is unstable, yielding $\text{H}_2\text{O} + \text{SO}_2$.

Pure hydrogen bromide can be made by warming a bromide with phosphoric acid:

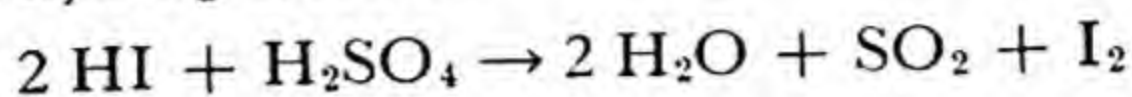


because phosphoric acid is not an oxidizing agent. Like sulfuric acid it has a high boiling point.

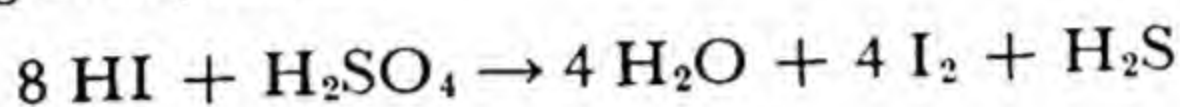
We might have expected also to make hydrogen iodide by warming an iodide with concentrated sulfuric acid:



Very little fuming in moist air shows the presence of but little hydrogen iodide. Much violet vapor is evolved that proves to be free iodine. As with the bromide, concentrated sulfuric acid oxidizes the hydrogen iodide:



A vile odor of rotten eggs indicates the presence of hydrogen sulfide (H_2S), so some molecules of sulfuric acid must have given up all four oxygen atoms for the work of oxidation. This really means that hydrogen iodide is a more vigorous reducing agent than hydrogen bromide:

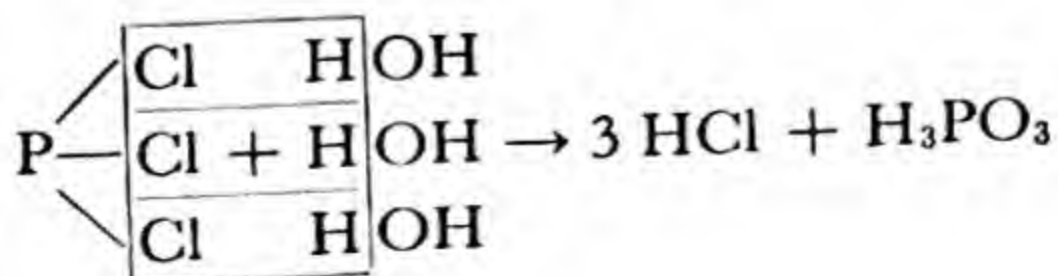
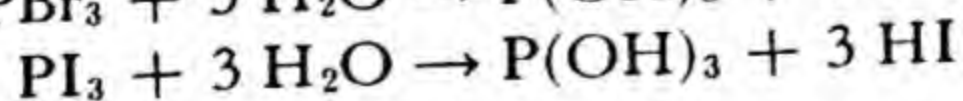
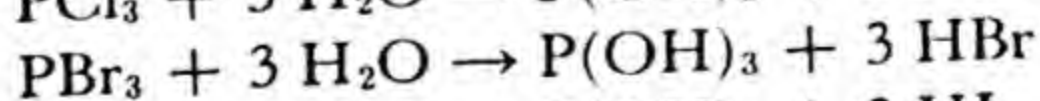
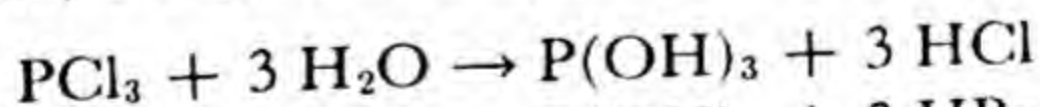


Therefore we discard the sulfuric acid method as unsuitable for hydrogen bromide or iodide. Phosphoric acid would be excellent, as it is not very volatile and is not an oxidizing acid, but unfortunately the action is too slow.

There is no oxidation of HBr if a slightly diluted solution of H_2SO_4 is mixed with a saturated aqueous solution of KBr and warmed. A similar method fails to make pure HI .

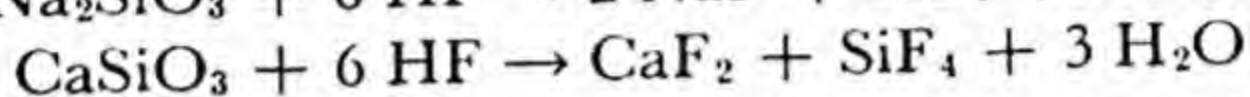
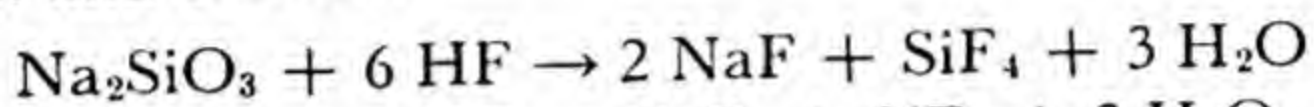
The difference in the ease of oxidation of hydriodic acid and hydrobromic acid is shown by the fact that at 100° a 25 per cent solution of sulfuric acid will oxidize the hydriodic acid, while 70 per cent sulfuric acid is necessary for oxidation of hydrobromic acid.

The Red Phosphorus Method. The red phosphorus method of preparation of hydrogen bromide and iodide, however, serves us very well. It is recalled that chlorine and phosphorus unite to form a chloride, PCl_3 , that is hydrolyzed by water:



ultraporous charcoal at 200°. Fully 99.3 per cent of the gases unite to form HBr. Without the carbon practically no reaction takes place. The formation of HCl and of HI is similarly catalyzed by carbon. Platinum also is an effective catalyst for these reactions.

Uses of the Acids. *Hydrochloric acid* is used in the preparation of metallic chlorides, and in the removal of oxide scale from steel about to be tinned or galvanized. Hydrobromic and hydriodic acids have little commercial use, but *hydrofluoric acid* is valuable because it etches glass. Common glass is a mixture of the silicates of sodium and calcium:



Bottles, thermometers, etc., are marked by covering with a film of paraffin, cutting through a design, and then exposing the vessels to the fumes or the liquid acid. The wax is not attacked but the glass is etched where the scratches expose it. Later the vessel is washed and the wax melted. A 30 per cent solution of the acid commonly is used. Rubber, lead, bakelite, or ceresin-wax bottles are the common containers, since this acid cannot be kept in glass bottles.

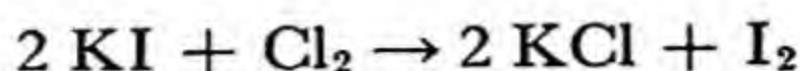
This acid is used in aiding glass polishers to make "cut" glass, in cleaning sand from metal castings, and in removing silica from straw used for hats so as to make the straw more flexible. The action on silica or sand is:



Anhydrous liquid hydrogen fluoride now has considerable use as a catalyst in the petroleum industry, in the manufacture of "Freon" and for certain secret military purposes. In the liquid form HF is not the correct formula but some multiple of it, a "polymer." It boils at 19.4° C.

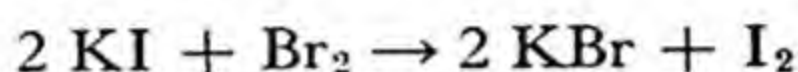
Hydrofluoric acid is also used in preparing synthetic cryolite (a mineral found only in Greenland and necessary in the electrolytic preparation of aluminum). Since this mineral is a double fluoride of sodium and aluminum it obviously may be prepared from Na_2CO_3 and $\text{Al}(\text{OH})_3$. What are the equations?

Tests for the Halogens. Free chlorine is recognized by its odor, its yellow color, and its ability to displace iodine from any soluble iodide:



If starch is present, the free iodine with the starch forms a blue compound (or solution).

Free bromine is known by its red-brown color, its odor, and its ability to displace iodine from any soluble iodide. The usual blue color with starch is produced:



Free iodine, with its violet-black color and its formation of a blue color when in contact with starch, is easily recognized. Furthermore, its solution in carbon disulfide shows a beautiful violet color.

A soluble chloride reacts with a solution of silver nitrate to give a white precipitate of silver chloride, that darkens in the light. A soluble bromide with silver nitrate gives insoluble yellow-white silver bromide. A soluble iodide with silver nitrate precipitates canary-yellow silver iodide. Furthermore, chlorine water displaces bromine from a bromide and iodine from an iodide.

Preparation of Salts. Illustrations of various methods of preparing salts are:

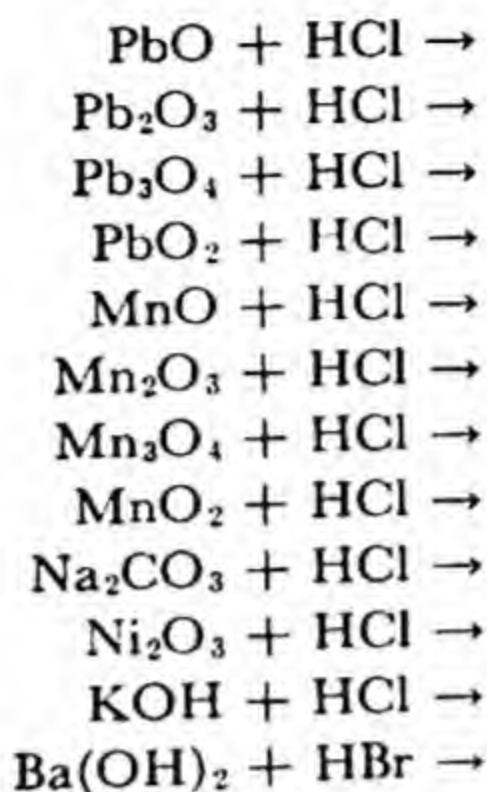
1. $\text{Ca} + \text{Cl}_2 \rightarrow \text{CaCl}_2$
2. $\text{Ca} + 2 \text{HCl} \rightarrow \text{H}_2 + \text{CaCl}_2$
3. $\text{CaO} + 2 \text{HCl} \rightarrow \text{H}_2\text{O} + \text{CaCl}_2$
4. $\text{Ca(OH)}_2 + 2 \text{HCl} \rightarrow 2 \text{H}_2\text{O} + \text{CaCl}_2$
5. $\text{CaCO}_3 + 2 \text{HCl} \rightarrow \text{H}_2\text{O} + \text{CO}_2 + \text{CaCl}_2$
6. $\text{CaSO}_3 + 2 \text{HCl} \rightarrow \text{H}_2\text{O} + \text{SO}_2 + \text{CaCl}_2$
7. $\text{Melt CaO} + \text{SiO}_2 \rightarrow \text{CaSiO}_3$
8. $\text{CaO} + \text{SO}_3 \rightarrow \text{CaSO}_4$
9. $\text{CaCl}_2 + \text{Na}_2\text{SO}_4 \rightarrow 2 \text{NaCl} + \text{CaSO}_4 \downarrow$

Exercises

4. When hydrogen chloride (in solution) is electrolyzed, equal volumes of hydrogen and chlorine are obtained. Also when equal volumes of hydrogen

and chlorine are combined, two volumes of hydrogen chloride are formed. How does this confirm Gay-Lussac's Law?

5. Balance:



6. How many liters of chlorine are released by heating 72 kg. of red lead, Pb_3O_4 , with enough hydrochloric acid to complete the reaction?
7. Make zinc chloride five ways. Equations. Make zinc sulfate four ways. Give four general methods of preparing any salt desired.
8. Suppose you wished to prepare 650 g. of hydrobromic acid solution containing 9 per cent by weight of HBr . Calculate the weights of the various compounds that you would use in its preparation.
9. How much (a) calcium sulfate and (b) hydrogen fluoride are formed by heating 42 g. of fluorspar with sulfuric acid?
10. You suspect the presence of a little HBr gas in the air of the laboratory. How could you prove that it is present?
11. Calculate the volume of 0.5 M sulfuric acid required for reaction with each of the following: 68 g. calcium oxide; 30 g. magnesium oxide; 125 g. aluminum oxide.
12. Suppose that tomorrow a new halogen is isolated with an atomic weight of 214. Describe its properties, how the hydro-acid is made, and the properties of the acid. Call the element "Doline" (Do) and the acid hydrogen dolide or hydro-dolidic acid (HDo).
13. Make a four-column chart on which you compare the four halogens in solubility, action on water, and other properties. Compare their hydro-acids in case of oxidation. Give tests for the four elements and the four acids.
14. Distinguish between a chloride, bromide, and iodide (white solids as given to you) by the results obtained on the addition of concentrated sulfuric acid.
15. Name some uses of HF .

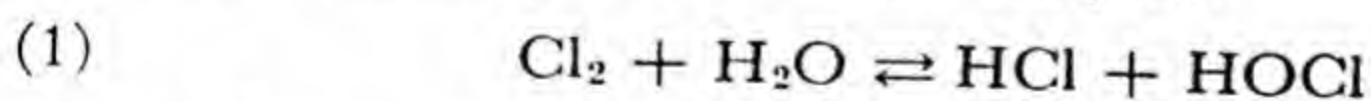
Chapter 18 THE OXYGEN ACIDS OF THE HALOGENS

NOMENCLATURE

HCl	Hydrochloric Acid	NaCl	Sodium Chloride	HBr	Hydrobromic Acid	HI	Hydriodic Acid
HOCl	Hypochlorous Acid	NaOCl	Sodium Hypochlorite	HOBr	Hypobromous Acid	HOI	Hypoiodous Acid
HClO ₂	Chlorous Acid	NaClO ₂	Sodium Chlorite	—	—	—	—
HClO ₃	Chloric Acid	NaClO ₃	Sodium Chlorate	HBrO ₃	Bromic Acid	HIO ₃	Iodic Acid
HClO ₄	Perchloric Acid	NaClO ₄	Sodium Perchlorate	—	—	HIO ₄	Periodic Acid

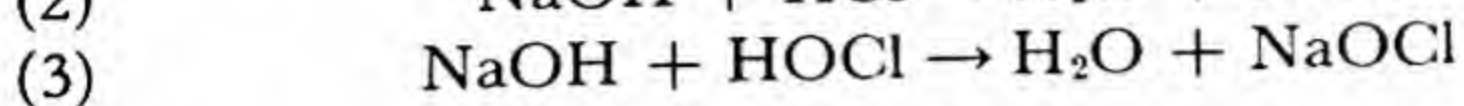
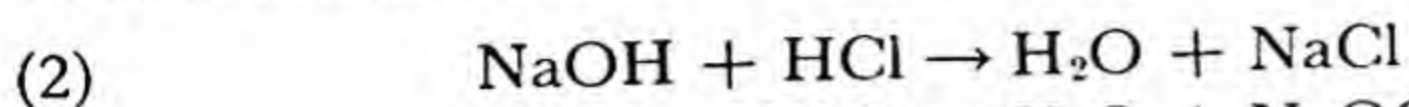
Chlorine and iodine do not combine directly with oxygen, but their oxides can be made by indirect methods. Bromine has no oxides, and fluorine forms no oxygen acid.

Hypochlorous Acid. The key reaction of this entire chapter has been studied in the chlorine chapter:



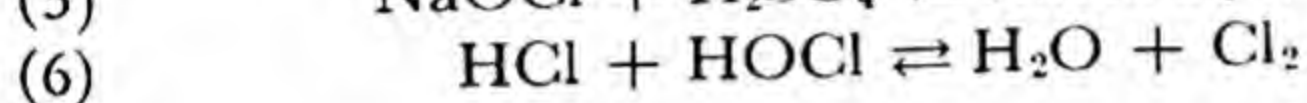
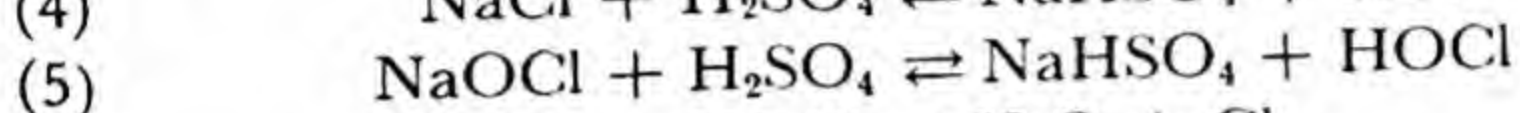
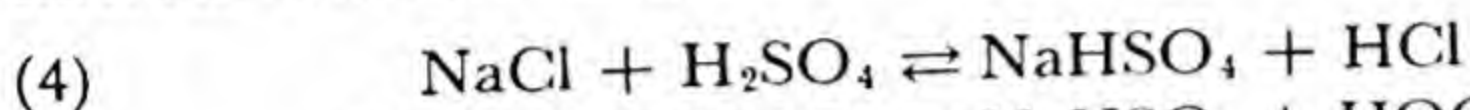
This is shown to be a reversible reaction by tests for acidity and for the presence of free chlorine. The presence of dissolved chlorine is indicated by the yellow color of the mixture and by the odor. The hypochlorous acid (HOCl) is a powerful oxidizing agent and so the equilibrium is disturbed toward the right by the presence of any oxidizable substance. Addition of a base also disturbs the equilibrium toward the right by conversion of the

two acids into salts. (The equilibrium condition in bromine water is disturbed in similar manner by addition of a base.)



In other words there is no free chlorine left in the solution after sufficient base has been added.

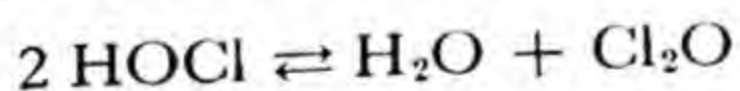
If to the mixture represented by equations (2) and (3) sufficient dilute sulfuric acid is added, both hydrochloric and hypochlorous acids are formed:



Reaction (6) inevitably follows (4) and (5). It is simply the reverse of (1). It is no wonder that chlorine can be detected after acidifying Javelle water (a solution of NaOCl and NaCl (see page 178)).

Hypochlorous acid is a more energetic oxidizing agent than oxygen. It bleaches by the oxidation of coloring matter and kills bacteria by oxidation. It will even decolorize iodine water by oxidation. Equations?

On being concentrated too far this unstable acid decomposes into water and its anhydride, chlorine monoxide:



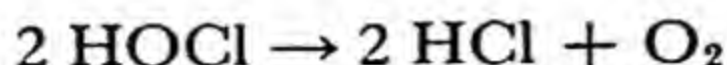
The sodium salt is also rather unstable but a mixture with trisodium phosphate is fairly stable.

An *anhydride* of an acid is an oxide that reacts with water to form the acid and it may be represented by the formula of the acid less the elements of water. SO_3 is the anhydride of H_2SO_4 . To get the anhydride of nitric acid we must subtract H_2O from 2HNO_3 .

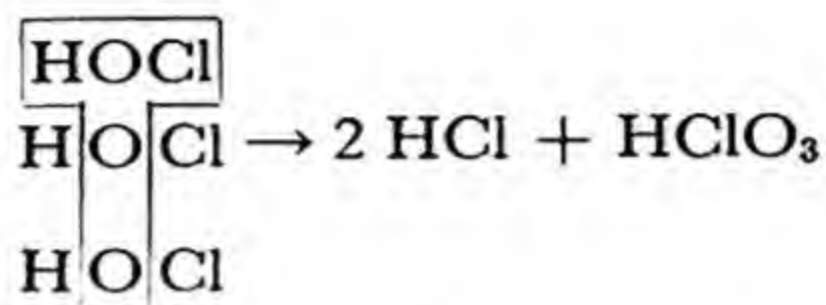
Exercise

1. What is the anhydride of carbonic acid (H_2CO_3)? Of phosphoric acid (H_3PO_4)? Of sulfuric acid?

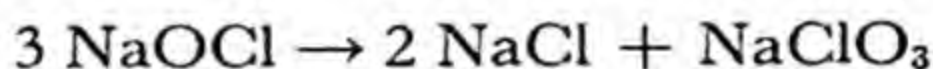
In the chlorine chapter we learned that hypochlorous acid decomposes slowly in the sunlight:



The free acid decomposes in another way, as shown by the equation below:



The sodium salt reacts in similar fashion, especially in a hot, concentrated, slightly acid solution, and sodium chlorate is formed rapidly:



This remarkable reaction reminds us of three brothers, each too poor to boast. But two self-sacrificing ones gave all their money to the third, enriching him to a degree that brought luster to the family name. This is most absurd, but gives a clear parallel to the auto-oxidation of the 3 NaOCl.

Potassium chlorate, useful as a solid oxidizing agent in fireworks and matches, is formed in similar fashion.

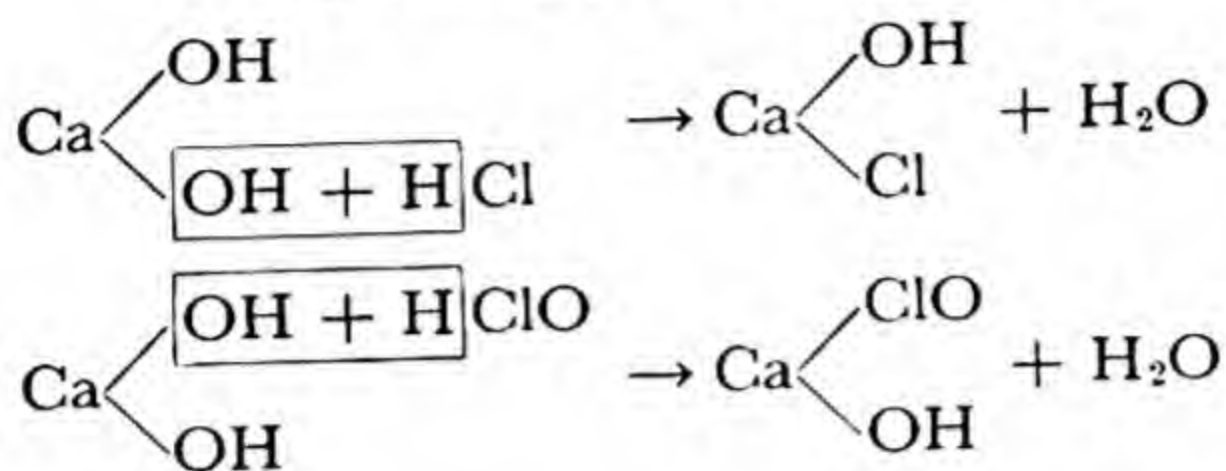
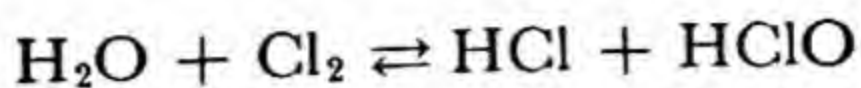
2. In what three ways can hypochlorous acid decompose?

Bleaching Powder. Lime (slaked into the hydroxide) may be used instead of sodium hydroxide to react with chlorine and, if this is done in the nearly dry form, a *bleaching powder* results. Tennant in Scotland, by the first use of bleaching powder (1799), changed the time for textile bleaching from months to days, later to hours.

Bleaching powder is sometimes called "chloride of lime," which should refer only to CaCl_2 . It was once thought to be a mixture of an equal number of molecules of CaCl_2 and $\text{Ca}(\text{OCl})_2$.

In 1935, by X-ray pictures, it was shown that bleaching powder is a mixture of basic calcium chloride and basic calcium

hypochlorite. $\text{CaCl}_2 \cdot \text{Ca}(\text{OH})_2 + \text{Ca}(\text{OCl})_2 \cdot \text{Ca}(\text{OH})_2$ represent the proportions:

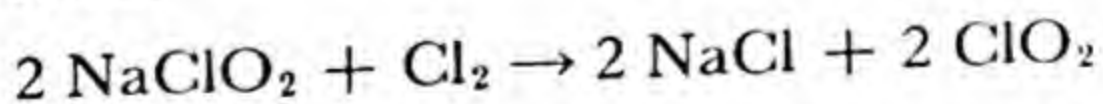


The best modern laundry practice discourages the direct use of bleaching powder and uses Javelle water made by the reaction between bleaching powder and sodium carbonate in solution. The insoluble calcium carbonate is filtered off leaving NaOCl and NaCl in solution. Equations?

3. Electrolyze a solution of NaCl in a beaker while stirring and evaporate to dryness. What have you? Remember that in making chlorine and sodium hydroxide we try to keep the anode and cathode solutions separated by a porous membrane. Also read page 209.

Chlorous Acid. This acid, HClO_2 , is of little interest but its salt, sodium chlorite, has just come into commercial production as a safe bleaching agent for textiles, paper, straw, and flour, with certain advantages over common bleaching powder. It does not weaken fibers.

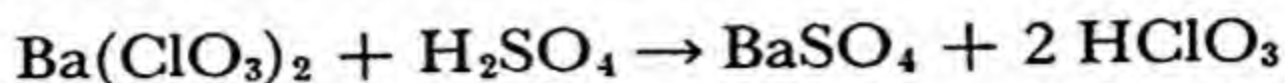
When chlorine is passed over dry sodium chlorite, NaClO_2 , **chlorine dioxide** gas is formed. It has 2.5 times the oxidizing power of chlorine.



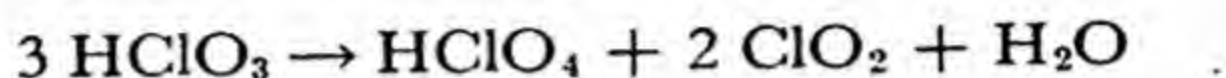
Chlorine dioxide is now used for bleaching flour, starch, soap, paper and textiles. It also improves the taste and odor of public water supplies and checks blue mold in citrus fruits. It is unstable and must be prepared as needed.

Chloric Acid. One of the most important of the oxygen acids of the halogens is chloric acid (HClO_3), a powerful oxidizing agent. It can be made by the action of dilute sulfuric acid on any

chlorate, preferably barium chlorate, because the by-product, barium sulfate, is insoluble and can be filtered off:



Addition of concentrated sulfuric acid to chlorates is dangerous, for the chloric acid formed is dehydrated yielding chlorine dioxide gas (explosive when hot):



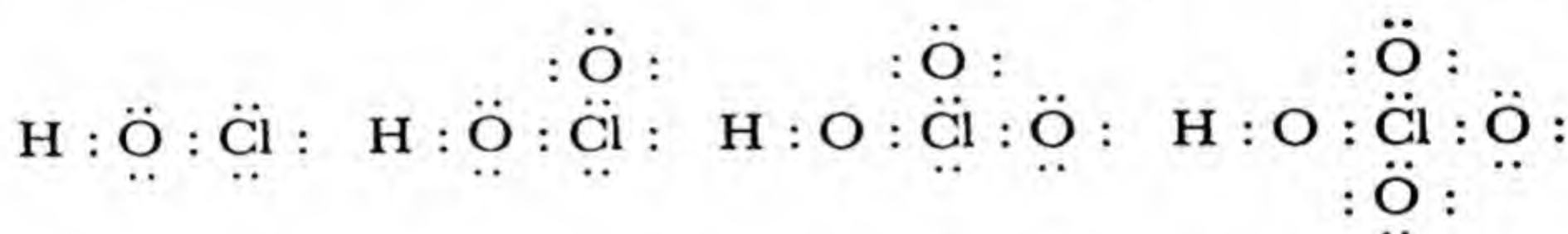
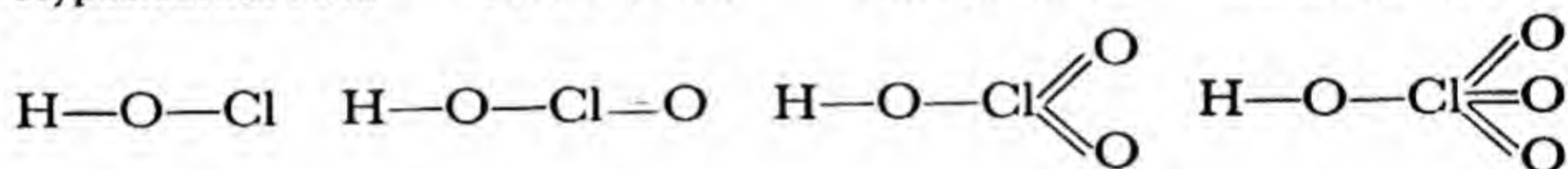
The *structural formulas* of the oxygen acids of chlorine are worth noting.

Hypochlorous Acid

Chlorous Acid

Chloric Acid

Perchloric Acid



When the outer electrons are written as above it is seen that, aided by sharing pairs, the chlorine and oxygen atoms have completed outer shells of eight. So far we have considered the valence number of chlorine as one, but here we see that it may also be three, five, or seven. Chlorine heptoxide (Cl_2O_7) indicates a valence number of seven as it should be in the anhydride of perchloric acid. Of what acid is I_2O_5 the anhydride?

Chlorates. More important than chloric acid is its potassium salt (KClO_3). This finds use as a convenient laboratory source of oxygen and in the manufacture of fireworks, matches, dyes, and explosives. It is such an effective source of oxygen that the results of its use are often startling and sometimes dangerous.

It is interesting to drop a splinter into a test tube one-third full of melted potassium chlorate. So vigorous is the oxidation of the wood that it burns brilliantly under the liquid, flames shoot out of the tube, and some spattering of hot liquid may result. Were the wood finely divided as sawdust or used as powdered charcoal, a dangerous explosion would result.

The most modern method of manufacture is to electrolyze potassium chloride, letting the solutions at the anode and cathode mix. This first produces the hypochlorite, but if the solutions are hot and concentrated the chlorate is the final product.

The Perchlorates. The perchlorates are prepared electrolytically by electrolysis of 60–70 per cent solutions of sodium hypochlorite, using iron cathodes. Anodic oxidation at high current density against smooth platinum anodes is the explanation of the change.

The most surprising property of perchloric acid and its salts is their comparative stability. Especially is this true of the perchlorates of Na, K, Ba, Sr, and Ca. Sodium chlorate is in extensive use as a weed killer but it is dangerous when mixed with oxidizable dust. The perchlorate is urged as a safer substitute yet the use of 70 per cent perchloric acid in the analytic oxidation of organic material has caused explosions. Hot concentrated perchloric acid is a powerful oxidizing agent and dehydrating agent. With proper precautions, its use is reasonably safe.

The Bromates and Iodates. Bromates and bromic acid, HBrO_3 , are similar to the chlorates and chloric acid. Sodium iodate is NaIO_3 .

Exercises

4. Suppose you electrolyzed 450 g. of potassium chloride in an apparatus so arranged that the chlorine set free at the anode would react with the potassium hydroxide formed at the cathode. What weight of potassium chlorate would be formed on boiling the solution to dryness?
5. When sufficient NaOH or other base is added to bromine water the red color disappears. Explain. Color reappears on acidifying. Why?
6. Why is it dangerous to add concentrated sulfuric acid to several grams of potassium chlorate?
7. Make out a list of all the oxidizing agents mentioned so far. Also a list of all the reducing agents.
8. If a mixture of sulfur and potassium chlorate were ignited (don't do it), what reaction would probably take place?
9. A water solution of chlorine is kept on the desk for a year in a clear glass bottle. What does it then contain?

Chapter 19 SODIUM AND SODIUM HYDROXIDE. BASES

Occurrence of Sodium. There is about as much sodium as potassium in the earth's crust, but most sodium minerals are soluble, whereas soluble potassium minerals are scarce. Sodium chloride is the starting point for most of our prepared sodium compounds. There are also important deposits of sodium nitrate, sodium sulfate, sodium carbonate, borax, and albite feldspar.

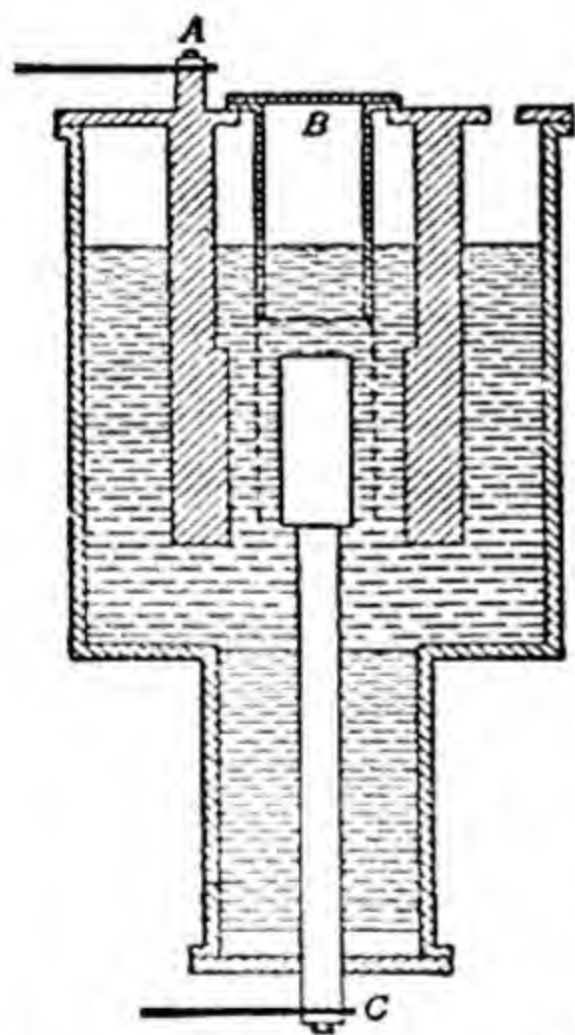
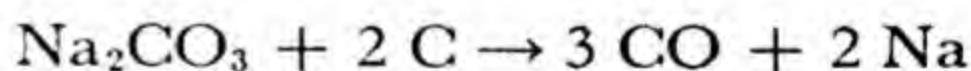


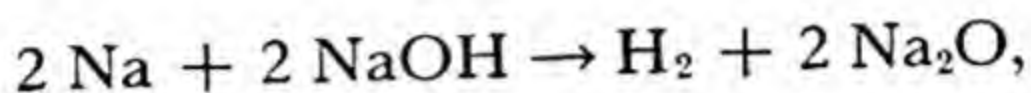
Fig. 80. Preparation of sodium by electrolysis of fused dry sodium hydroxide.

Preparation. Sir Humphry Davy was the first to prepare sodium. He electrolyzed moist sodium hydroxide and collected the metal at the cathode. In the same year (1807) he made potassium from its hydroxide. The high cost of electricity for many years hindered the commercial development of Davy's discovery. During this period the metal was prepared by reduction of the carbonate or hydroxide:



With cheap electricity Davy's method was revived, in modified form. Castner's method, not much used now, is to electrolyze fused sodium hydroxide in an iron vessel with the cathode (an iron rod) under a bell or inverted iron box (Fig. 80). The metal floats to the surface under this bell and is protected from the air

by the hydrogen which is also liberated at the cathode. From time to time the hydrogen escapes by lifting the lid of the bell. Oxygen is released at the iron anodes. A wire gauze keeps the drops of sodium in the cathode compartment. Good commercial practice calls for a temperature as close to the melting point of the hydroxide (300°) as possible. At 325° the sodium is lost by reaction with the hydroxide.



while at 300° the yield is good.

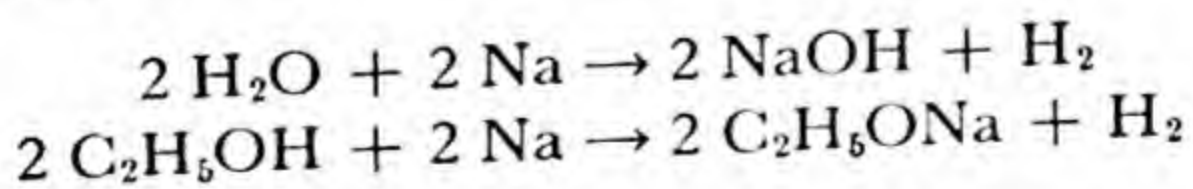
Sodium hydroxide melts at 300° and sodium chloride at 800° , so it is evident why the hydroxide is electrolyzed more easily.

The Downs electrolytic cell is now much used for production of metallic sodium. In construction it is rather similar to the old Castner cell but in operation differs, for the fused electrolyte is sodium chloride to which has been added enough sodium carbonate to lower the melting point from 800° to 600° .

The growing demand for metallic sodium is evidenced by its present shipment in tank cars containing several tons. The world uses many thousands of tons yearly.

Sodium is more than a "laboratory" chemical. It is an important commodity for use in a number of large-scale industrial processes. It finds commercial use in the manufacture of heavy and fine chemicals, dyestuffs such as indigo, anti-knock compounds, and in metallurgy.

Properties. Sodium is silver-white, soft, and lighter than water. It melts at 97.6° and boils at 880° . Sodium is very active chemically, and reacts violently with water. In a milder way it displaces hydrogen from alcohol:



It slowly unites with oxygen at room temperatures and burns if heated in oxygen or air forming both the monoxide, Na_2O , and the peroxide, Na_2O_2 . With the halogens reaction readily occurs. Also it reacts with ammonia, NH_3 , to form sodamide, NaNH_2 .

Sodium amalgam is a solution of sodium in mercury (really an alloy). With plenty of sodium the solution is a solid. Its action on water is moderated by the mercury, so the alloy is a useful reducing agent. An alloy of lead and sodium is quite similar and is used in the manufacture of ethyl fluid for gasoline.

Sodium Hydroxide, NaOH. This important substance is a white, brittle solid. It is very soluble in water and is quite deliquescent. Sticks of sodium hydroxide exposed to the air rapidly

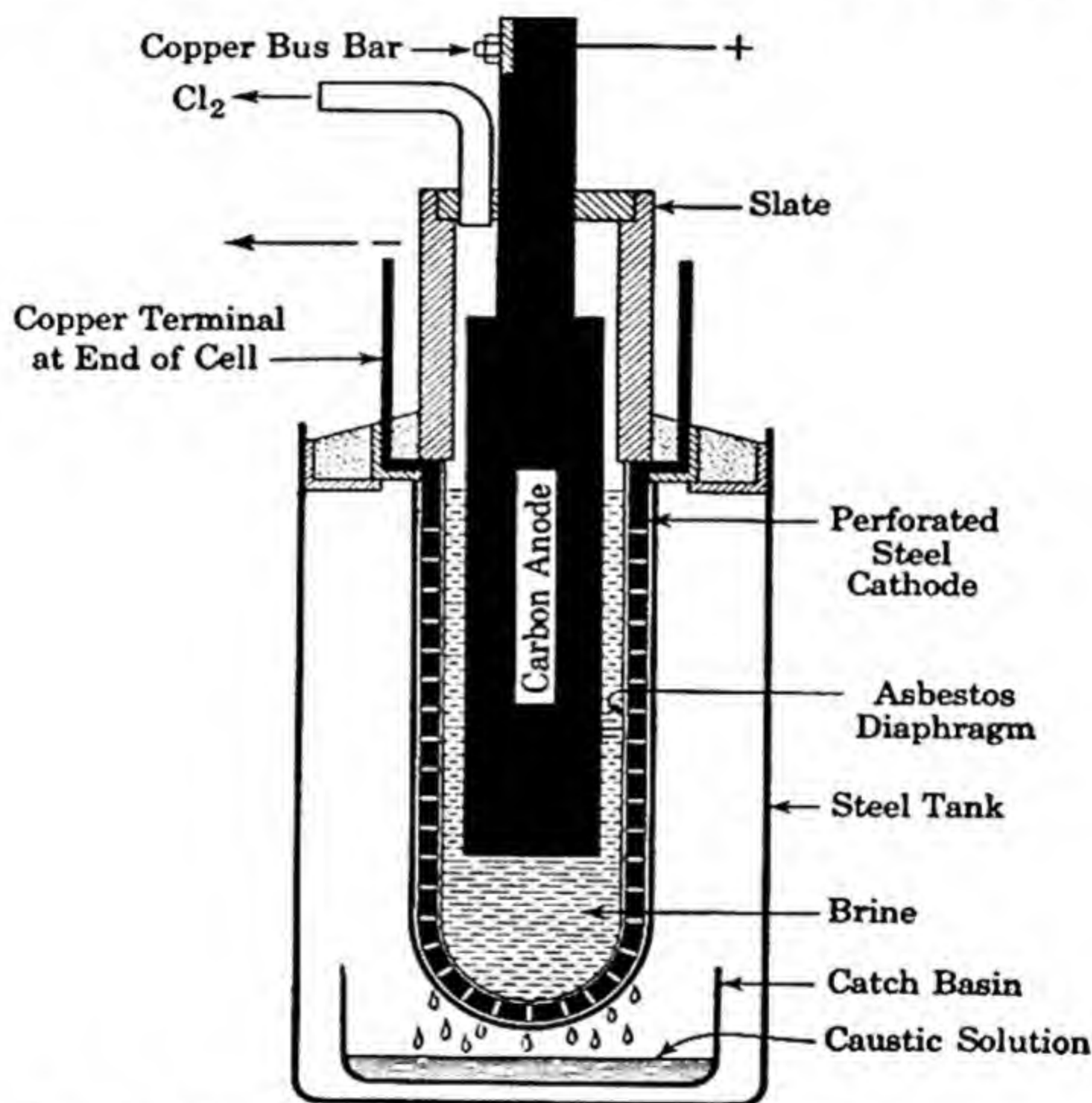
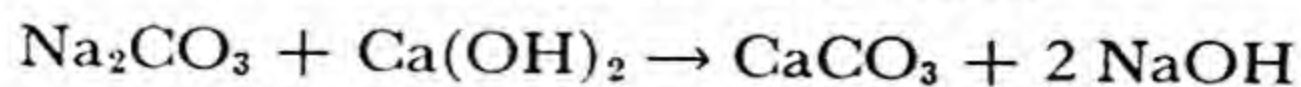


Fig. 81. Nelson cell for the preparation of sodium hydroxide.

take up water and carbon dioxide. For this reason it is often used in analysis as a drying agent and to absorb carbon dioxide. To purify the hydroxide it is sometimes dissolved in alcohol. Any carbonate present remains undissolved. Much sodium hydroxide, nearly half the total, is made commercially by treating boiling soda solutions with slaked lime in some excess:



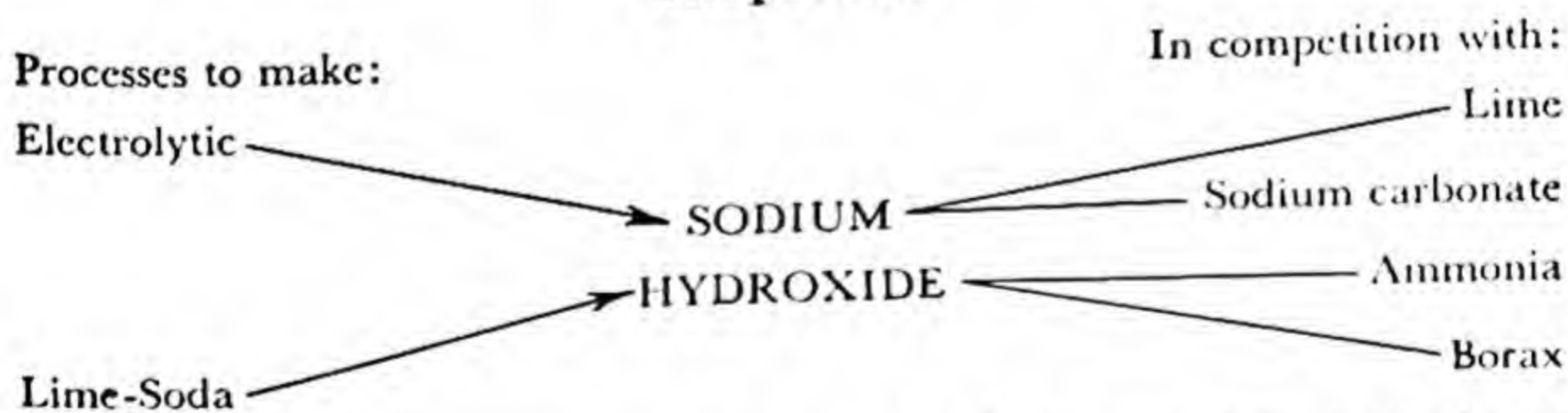
The precipitated calcium carbonate is filtered off, calcined to form more lime, and the filtrate is concentrated. The leading commercial method is the electrolysis of sodium chloride solutions, and by this method nearly 1,600,000 tons have been produced in a recent year. The total for the two methods is 2,600,000 tons.

The Nelson cell (Fig. 81) is one of the leading cells. It is of the diaphragm type. The graphite anodes, where the electric current enters the cell, are separated from the cathode, a perforated steel plate, by a porous diaphragm of asbestos. An inverted box of slate over the anodes collects the chlorine. The cell body is a steel tank with an outlet for the sodium hydroxide solution. A current of steam may be led through the cathode compartment to speed up diffusion. Salt brine flows steadily into the anode compartment. The outflowing solution contains 10 to 12 per cent sodium hydroxide and 14 to 16 per cent salt, which is precipitated by partial evaporation. This is a simple matter because salt is much less soluble than the hydroxide. The cells are rated at 1000 amperes and the voltage drop averages 3.7 volts. At least 2.3 volts are required to secure any decomposition of sodium chloride in water.

In the diagram an inlet at the top for salt brine and an outlet for hydrogen gas evolved are understood.

If the sodium hydroxide were not steadily removed it would itself be electrolyzed (wasted electricity), yielding sodium (and consequently NaOH) at the cathode and oxygen at the anode.

Competition



The hydrogen released at the cathode is sometimes made to unite with the chlorine from the anodes, forming hydrochloric acid.

The Germans have revived and improved the obsolete Castner sodium amalgam process of making sodium hydroxide. In this cell, electrolysis of sodium chloride solution proceeds with a pool of mercury at the bottom as cathode. Sodium amalgam forms, is removed under a partition dipping into mercury, becomes the

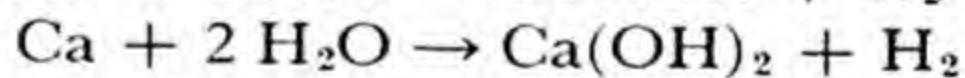
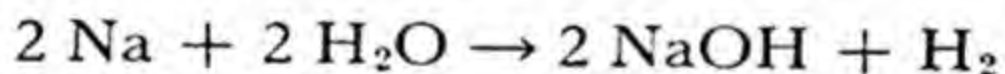
anode in a second electrolytic compartment with a solution of sodium hydroxide. Metallic sodium ions leave the anode to form NaOH with OH^- ions of water. Water reacts directly with sodium amalgam but too slowly. A 30–50 per cent concentration of pure sodium hydroxide is formed.

DISTRIBUTION OF SODIUM HYDROXIDE IN THE UNITED STATES, TYPICAL YEAR

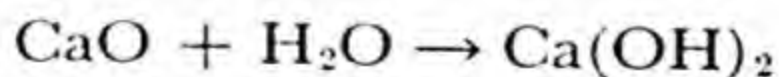
INDUSTRY	TONS
Soap	110,000
Chemicals	460,000
Petroleum refining	160,000
Rayon, and cellulose film	455,000
Lye and cleansers	120,000
Exports	130,000
Textiles	105,000
Rubber reclaim	27,000
Vegetable oils	20,000
Pulp and paper	130,000
Miscellaneous	363,000
Total	2,080,000

In 1947 this total became 2,600,000 tons.

Bases. Basic hydroxides are formed when such metals as sodium, potassium, or calcium react with water:

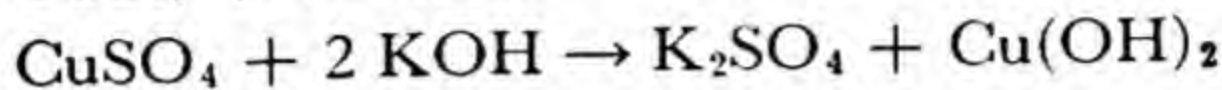
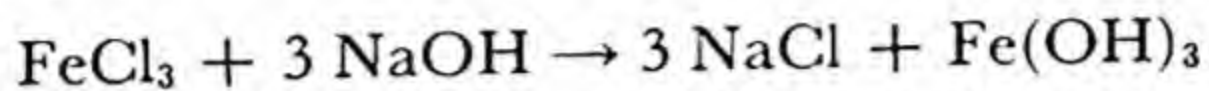


Commercially, however, the most active bases, the so-called alkalis, sodium hydroxide and potassium hydroxide, are made by cheaper methods. Calcium hydroxide is most cheaply prepared by the addition of water to quicklime, CaO , itself obtained by calcining CaCO_3 , limestone.

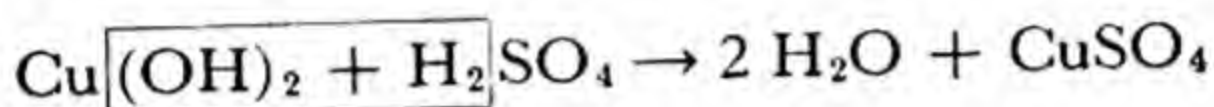
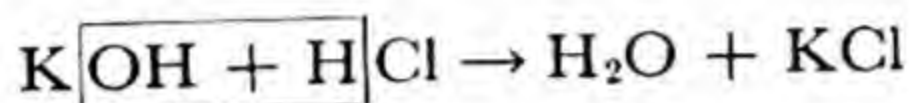


All the basic hydroxides contain OH groups attached to a metal. (Some other types of compounds also contain OH groups but not attached to a metal.) Many organic compounds without —OH groups react with acids and are called organic bases since they, like —OH groups, will combine with acidic hydrogen (we say they accept protons).

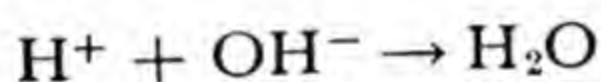
Insoluble Bases. Most of the metallic hydroxides are insoluble, like ferric hydroxide, $\text{Fe}(\text{OH})_3$. They are conveniently prepared by addition of a solution of any soluble base to a solution of some salt of the metal in question:



Reaction of Bases with Acids. All bases react with acids to form water and a salt, a process called neutralization:



The essential reaction really is



where the OH^- ion (from the base) accepts the H^+ ion, or proton, from the acid.

It is a common error to think of all hydroxides as bases, yet some are acids and some act as base or acid depending upon other substances present. An OH group attached to a metal as in KOH is basic, but if attached to a non-metal as in $\text{HO}-\text{NO}_2$ (nitric acid, HNO_3), it is acidic.

NaOH strong base

Ca(OH)₂ mild base

Zn(OH)₂ may act as base or acid, H_2ZnO_2

B(OH)₃ is a weak acid (boric), H_3BO_3

Si(OH)₄ is an acid (silicic), H_4SiO_4

SO₂(OH)₂ is sulfuric acid, H_2SO_4

Exercises

1. What volume of hydrogen at 25° C. and 740 mm. may be liberated from water by the sodium formed by the electrolysis of 21 kg. of NaOH?
2. What weight of cupric hydroxide is formed by the interaction of 75 g. of copper sulfate ($\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$) with excess of sodium hydroxide in aqueous solution?

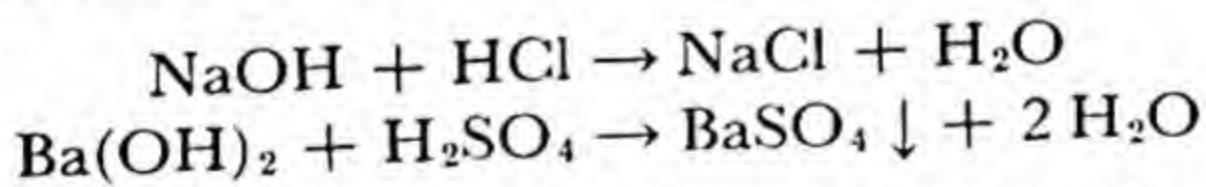
3. In a chlorine plant 80 tons of sodium chloride in solution were electrolyzed daily. (a) Calculate the weight of sodium hydroxide formed. (b) What volume of hydrogen was liberated?
4. How many grams of sodium hydroxide would be required to form 750 ml. of a molar solution? How many to form 10 liters of a normal solution?
5. What weight of sodium hydroxide is needed to neutralize 400 ml. of a 0.5 normal solution of sulfuric acid?
6. What weight of 90 per cent pure $\text{Ca}(\text{OH})_2$ is required to convert 8 kg. of $\text{Na}_2\text{CO}_3 \cdot 10 \text{H}_2\text{O}$ into sodium hydroxide?
7. How many grams of sodium hydroxide result from the action of 650 grams of sodium peroxide, Na_2O_2 , with water?

Chapter 20 IONS AND ELECTROLYSIS

Acids, Bases, and Salts. Acids all contain hydrogen, replaceable by active metals, although not all hydrogen compounds are acids, sugar for example. Acid solutions in water ordinarily taste sour, turn blue litmus red, release carbon dioxide from carbonates, and react with most metals with the displacement of hydrogen.

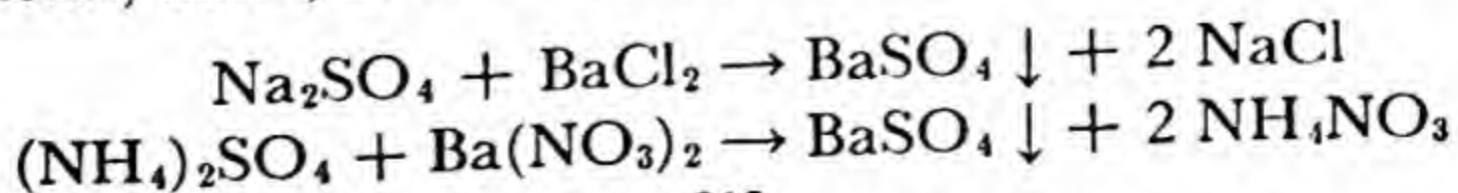
The common bases are compounds of a metal with oxygen and hydrogen. In water solution they turn red litmus blue, have a characteristic taste, and feel soapy. Such metallic hydroxides as those of sodium, potassium, and calcium (NaOH, KOH, Ca(OH)₂) have already been mentioned.

A salt or its equivalent is formed by the reaction between an acid and a base, the other product being water. Of course the actual salt is obtained only after evaporation of the water.



Here the sodium chloride and barium sulfate, remaining as solids after evaporation of the water, are salts. More exact definitions of acids, bases, and salts will be given a little later. Salts may be formed in several other ways.

The examples of double decomposition already studied (see page 179) show an apparent interchange of groups or radicals when acids, bases, or salts are mixed in aqueous solution.



The easy and instant exchange of partners in such reactions leads to the suspicion that the radicals were already separated in the solutions before they were mixed.

By the use of the X-ray we have already learned that in solid crystals of salts and of some strong acids and bases these very radicals or groups, so familiar in many reactions, exist as units geometrically arranged in the space lattice of the crystal. Furthermore, we know that when sodium chloride, for example, is melted or fused it conducts electricity readily and that metallic sodium appears at the negative pole (cathode) while chlorine is evolved at the positive pole (anode). Obviously in such a liquid electrically charged atoms must have been present to carry the current and there must have been both positive and negative atoms in order to account for the attraction of different atoms to different poles. Similar statements may be made concerning fused sodium hydroxide, lead chloride, and many other acids, bases, and salts.

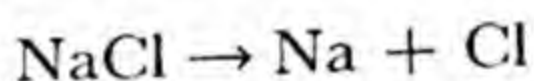
In a solid crystal of sodium chloride the electrical attraction between oppositely charged atoms (or groups) is too great to permit their movement to cathode and anode. No current passes. However, with the aid of heat the solid melts and the charged atoms or groups become mobile or fluid, and are able to carry a current.

Here we need to stress non-mobility of charged atoms or radicals in the solid and mobility in the melted solid.

The Arrhenius Theory of Ionization. Arrhenius of Sweden as a young man reasoned deeply about the fact that acids, bases, and salts in water solution all conduct electricity and are decomposed in the process. No other substances dissolved in water act in this way. He did not have, in 1887, the benefit of X-ray photographs revealing crystal structure (that came in 1913) nor did anyone in 1887 know about electron transfer in chemical reactions.

Arrhenius did know, however, of the *abnormally large values for freezing-point lowering, boiling-point rise, and osmotic pressure of aqueous solutions of acids, bases, and salts*. A solution of a gram-molecular weight of sugar, glycerine, etc., in 1000 g. of

water freezes at -1.86° . It makes no difference whether heavy sugar molecules or light alcohol molecules are dissolved, the only consideration is *number of dissolved particles*. Doubling the concentration practically doubles the freezing-point lowering. After observing this it is astonishing to learn that a solution containing one gram-molecular weight of sodium chloride per 1000 g. of water freezes at a temperature approaching *twice* 1.86° below zero (3.52°). Since this solution apparently contains exactly the same number of molecules as the sugar solution (a gram-molecular weight of each taken) and since the only influence on freezing-point lowering is *number of dissolved particles*, he was forced to the only possible conclusion, namely, that some of the sodium chloride molecules must have broken down, or dissociated into smaller particles, thus accounting for more particles than the original number of molecules. Now there is only one way for such a simple compound to dissociate, for there are only two atoms in each molecule of sodium chloride:



Obviously, if all the salt molecules split into two parts, the original number of molecules would be doubled and the solution would freeze at exactly $2 \times 1.86^{\circ}$ below zero. This complete dissociation is approximated only in very dilute solutions. Evidently the less water present the less the dissociation and with no water (dry salt) only molecules are found. Our present knowledge corrects this part of the classical theory.

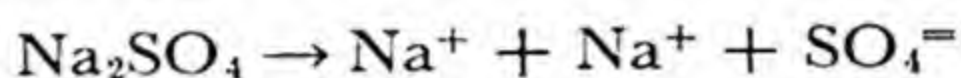
The student at once admits the necessity of accounting for more particles than indicated by a gram-molecular weight and admits that this explanation accounts for them, but he doesn't see how ordinary sodium can exist in contact with water. For that matter he is skeptical about the presence of elemental chlorine in salt water. Chlorine water is greenish yellow, poisonous, and a powerful oxidizing agent, and he knows by experience that salt water has none of these properties. He remembers that metallic sodium reacts violently with water, but there is nothing exciting to be seen when salt is dissolved in water.

The reply by Arrhenius to his critics was that this was not

common sodium metal but electrically charged sodium atoms ("ions") and that the chlorine was not ordinary chlorine but charged chlorine atoms (ions) with entirely different properties. Solutions of copper salts are blue due to the presence of charged copper atoms (ions) while common copper is red and insoluble.

He must have conceived the idea of electric charges on these ions from observations of the conductivity and electrolysis of water solutions of acids, bases, and salts.

A solution containing 1000 g. of water and one gram-molecular weight of sodium sulfate has a freezing-point lowering approaching, but not equal to, three times 1.86° . The inference is that each conventional molecule dissociates into three parts, probably:



The sulfate group does not disintegrate, for the freezing point of a solution of copper sulfate (CuSO_4) indicates the formation of only two parts per molecule, one of course being copper and the other the sulfate group. In all these dissociations the same radicals appear as those taking part in double decomposition—a very significant point.

Ionization Equilibrium. Another annoying question propounded to Arrhenius by his critics was this: if oppositely charged ions exist in the same solution, free to move, why do they not attract and discharge each other? They do, he replied, but as fast as they unite to form new molecules some other molecules ionize and we merely have a condition of ionic equilibrium which can be disturbed like any other equilibrium:



This method of writing the equation shows that there are both molecules and ions present. In more dilute solutions the percentage of molecules ionized is greater. This seems reasonable, for dilution keeps the ions farther apart, but has no effect on the action of molecules in breaking apart.

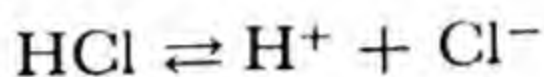
Our present knowledge revises this theory of Arrhenius but the classical theory should be considered here as it was in 1887.

Phrasing the classical theory in formal terms, "Acids, bases,

and salts in aqueous solution dissociate into atoms or groups of atoms which carry charges of electricity."

There is no excess of either positive or negative electricity on the ions dissociating from each molecule of an electrolyte. That is, there must be equal numbers of positive and negative charges on the anions and cations.

How else can we explain the *electroneutrality of solutions*? The salty ocean is neither positive nor negative, otherwise there would be very little ocean bathing. If we allow one positive charge to a hydrogen ion (H^+), then there must be one negative charge to a chloride ion (Cl^-) and the ionization of hydrogen chloride is:



Electrolysis. Although water was decomposed by the electric current as early as 1800 (Nicholson and Carlisle), most of our knowledge of electrolysis, and its terms, we owe to Faraday, the great English chemist and physicist.

When two metallic plates (electrodes) are placed in a solution and connected with a source of current we have an electrolytic cell. If a lamp is placed in the circuit, as in Fig. 82, we can observe by its glow when current is passing. An ammeter measures current more accurately. Place the electrodes in pure water and connect with the ordinary lighting circuit. The failure of the lamp to glow shows that little or no current passes. Evidently water is a poor conductor. Now add sugar or glycerine or alcohol to the water and stir. Even these solutions do not conduct the current. But add dilute sulfuric acid or some soluble salt or base and the lamp glows. In fact any acid, base, or salt dissolved in the water of the cell described will conduct the current. The remarkable fact is that *only acids, bases, and salts* (which we therefore call *electrolytes* or *ionogens*) will do this; all other substances are called non-electrolytes.

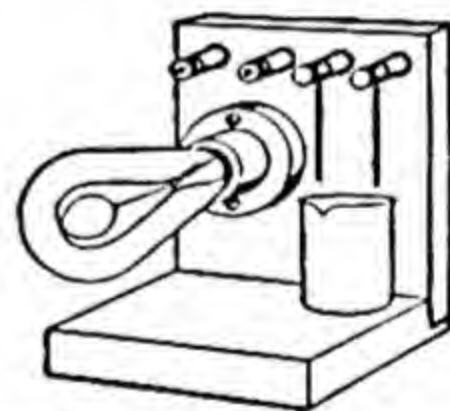


Fig. 82. A conductivity test.

Suppose in the cell of Fig. 83 we use a solution of hydrochloric acid and pass a direct current through the circuit. The "current of electricity" is merely the passage of a stream of electrons along a conductor. Unfortunately the direction of flow was wrongly indicated before we understood anything about a stream of electrons. The electrode through which the current always has

been considered to enter, but through which the electrons leave, is called the *anode* and the one by which the current leaves, or electrons enter, the *cathode*. Ions attracted to the anode are called *anions* while those attracted to the cathode are termed *cations*. The passage of the current merely keeps the anode positively charged and the cathode negatively charged. Hydrogen escapes at the cathode and chlorine at the anode. In other words, hydrochloric acid is electrolyzed. Hydrogen ions from the entire

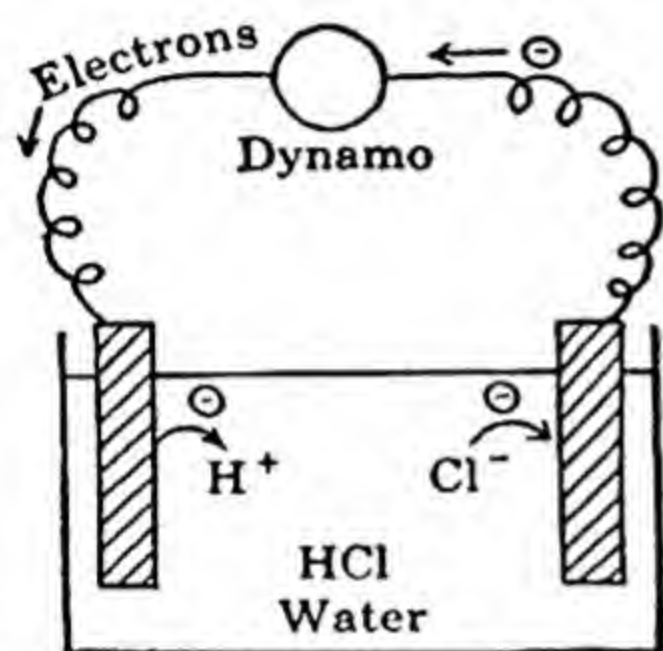


Fig. 83. Electrolysis of hydrochloric acid.

solution travel to the cathode and are there discharged. Why, unless they are attracted? The cathode is a negatively charged strip of metal and consequently attracts oppositely charged bodies. The conclusion is that the hydrogen ion is simply an atom carrying a positive charge of electricity. In this form it is soluble in water. On contact with the negative electrode it receives an electron from the circuit, its charge is neutralized, and the plain hydrogen atoms

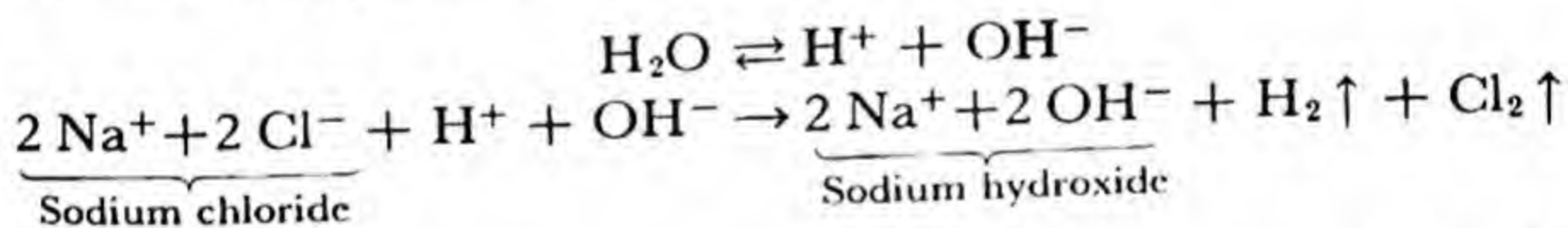
then unite in pairs to form ordinary hydrogen gas molecules, which escape. The chlorine ions move from all parts of the solution to the anode, or positive electrode. This attraction must be due to the presence of a negative charge on the chlorine atom. On contact with the electrode the charge on the chlorine atom is neutralized, that is, it gives its extra electron to the pole and common chlorine escapes and may be detected by the usual tests. Both the hydrogen and chlorine are *primary products of electrolysis*.

When sulfuric acid is electrolyzed, its hydrogen is liberated at the negative electrode, as with all acids, but the uncharged sulfate radical is not found as a molecular substance at the positive electrode. Instead, oxygen escapes. If the experiment is performed in a U-tube, it can be shown that sulfuric acid accumulates around the positive electrode and diminishes in concentration around the other electrode. Evidently the sulfate radical is attracted by the positive electrode because of the negative charge carried by the radical.

By one explanation, often given, it is not the $\text{SO}_4^{=}$ ion that is discharged at the anode but the OH^- ion (from ionization of water, slight though it is). The OH^- ion gives up its electron more readily to the anode than the $\text{SO}_4^{=}$ ion does. These OH^- ions after discharge unite in pairs to form water and oxygen gas.

Copper sulfate is electrolyzed to produce a red deposit of metallic copper on the cathode and the escape of oxygen at the anode. Sodium iodide, on electrolysis, shows the color of iodine at the anode and the solution yields the usual blue with a drop of starch paste. At the cathode hydrogen escapes, and if a drop of colorless phenolphthalein solution is added a splendid pink color develops, indicating the formation of a base. Sodium hydroxide is the only one possible.

According to one theory, it is easier to discharge the H^+ ions of water at the cathode than to discharge Na^+ ions. Therefore the Na^+ ions are paired off around the cathode with an equivalent number of OH^- ions coming from the slight ionization of water, and sodium hydroxide results:



In answer to this theory, held by so many chemists, it may be stated that with very weak currents of electricity and in very dilute solutions this explanation may apply but, when larger currents are passed in more concentrated solutions, there are not enough H^+ ions and OH^- ions from the incredibly minute ionization of water to carry the current. Then Na^+ ions, K^+ ions, SO_4 ions, NO_3^- ions, etc., may actually be discharged. Subsequent reaction with water yields NaOH , KOH , H_2SO_4 , HNO_3 , etc.

Iron ions may be discharged at the cathode from a weakly acid solution of iron salts, yet hydrogen ions are easier to discharge than the iron ions. This is astonishing, although true, because making a solution distinctly acid increases a million times or more the actual number of H^+ ions naturally present in water.

Furthermore it is well known that sodium, potassium, calcium, and other such ions are discharged on a mercury cathode, forming amalgams from which mercury can be distilled leaving the metallic sodium, etc. By the theory just quoted only hydrogen should have been discharged against the mercury cathode, a condition quite contrary to fact. This has been answered by stating

that the discharge potential of H^+ on a mercury cathode is higher than on other metals.

The oxidation effect at the anode of an electrolytic cell through which current is passed (not a primary cell which generates current) is used commercially in the preparation of various substances. Conversely, reduction takes place at the cathode and may be utilized commercially.

The Electron Transfer Explanation of Electrolysis. In the electrolysis of a water solution of HCl the H^+ ion is attracted to the cathode and there accepts one electron, thus becoming neutral hydrogen, insoluble in water. At the same time one electron is given to the anode by a Cl^- which then becomes neutral chlorine. The electrons are carried through the solution by the negative ions, given up at the anode, and driven by the dynamo along the metallic circuit to be presented to positive ions at the cathode. This is electrolysis. Compare with the electron concept of chemical reactions presented on pages 27, 111, and 174.

Faraday's Law.¹ Faraday gave us an experimental basis for ascribing a definite number of charges to each ion. He found that when a gram-equivalent weight of any metal or hydrogen has been liberated from a compound by electrolysis, exactly 96,500 coulombs of electricity have passed through the solution.

Faraday's laws of electrolysis (1833-34) are fundamental.

FIRST LAW: *The mass of any substance liberated at an electrode during electrolysis is proportional to the quantity of electricity passed through the electrolytic cell.*

SECOND LAW: *When the same quantity of electricity passes through different electrolytes, the masses of the substances liberated at the electrodes are proportional to their chemical equivalents.*

For example, 96,500 coulombs of electricity can set free from electrolyte solutions gram-equivalent weights of H (1.008 g.), of Ag' (107.88 g.), of Cu'' $\left(\frac{63.54}{2} \text{ g.}\right)$, and of Fe''' $\left(\frac{55.85}{3} \text{ g.}\right)$. Of

¹ The coulomb is the unit of quantity of electricity, as the liter is a unit of quantity of fluids.

course equivalent quantities of the negative ions are being discharged at the same time in electrolysis. That is, one gram-equivalent weight of hydrogen chloride is decomposed by 96,500 coulombs of electricity, for this means that one gram-equivalent weight of hydrogen and one gram-equivalent weight of chlorine are released simultaneously.

Electrolysis is merely an attraction and discharge of ions, so there must be 96,500 coulombs, a faraday, of electricity on each

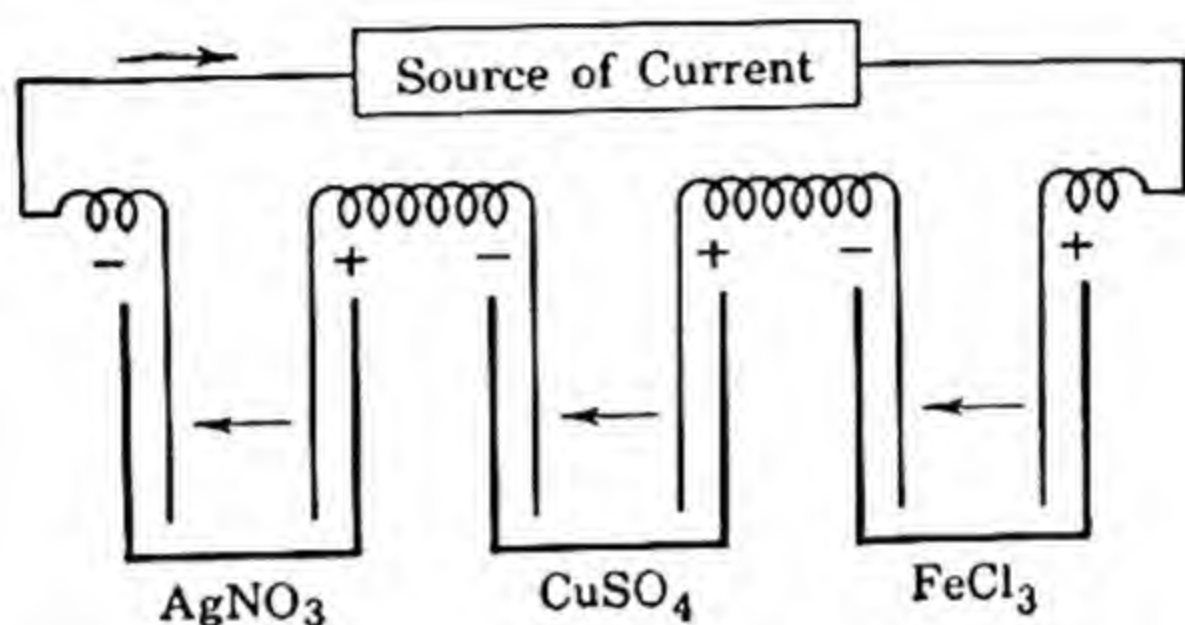


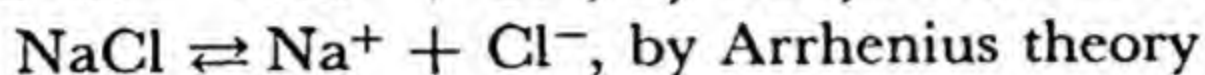
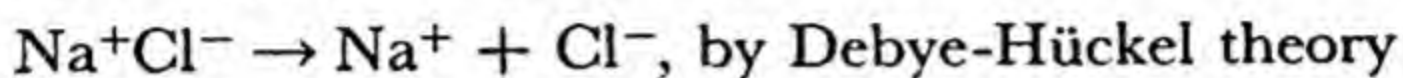
Fig. 84. On passing the same current of electricity through the solutions shown, equivalent quantities of silver, copper, and iron are deposited on the cathodes.

gram-atomic weight of hydrogen ions or of silver ions. But this quantity of electricity discharges only half of one gram-atomic weight of copper $\left(\frac{63.54}{2} \text{ g. Cu}\right)$, so there must be $2 \times 96,500$ coulombs on a whole gram-atomic weight of copper ions and, by similar logic, $3 \times 96,500$ coulombs on a whole gram-atomic weight of ferric ions.

MODERNIZATION OF THE ARRHENIUS THEORY

Complete Ionization. About 1922 Debye and Hückel suggested that in dilute solution the strong electrolytes (those that in water solution conduct strongly) are completely ionized. We are all agreed that in solid form salts and many such acids and bases have a crystal lattice of ions as revealed by X-ray photographs and by conductivity of many fused electrolytes. We also have good evidence for believing that these ions were formed by electron transfer in previous reactions.

Contrary to the belief of Arrhenius, then, we know now that ionization in many strong electrolytes took place long before solution in water or other solvent. The water merely separates ions already in the solid, by attracting these ions and by tending to insulate them against recombination:



Two limitations must be noted at this point. In a concentrated solution of HCl there certainly are many molecules, for they are observed coming off the surface as gaseous HCl. Probably in all concentrated solutions there are countless collisions of oppositely charged ions with temporary formation of ion pairs such as Na^+Cl^- . Such a pair may be termed a *conventional molecule* with the same composition as any larger amount.

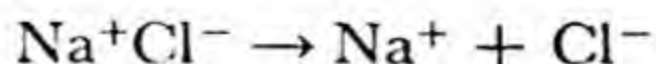
If this phrase is not helpful we may state that Na^+Cl^- represents the composition of any quantity of this substance. It is interesting to note here that when sodium chloride is vaporized actual gaseous molecules are formed.

The second limitation is concerned with weak electrolytes, which are poor conductors in water solution. These are not completely ionized and an equilibrium between molecules and ions does exist just as postulated by Arrhenius. Consider acetic acid which, in 0.1 N concentration, is only about 1.3 per cent ionized as calculated from freezing-point lowering and from electrical conductivity:



This equilibrium is disturbed by a change in concentration or by the removal of the H^+ ion (easily managed with a base). In the latter event the equilibrium is displaced to the right and eventually (in fact, quickly) all the molecules dissociate into ions. There are many weak electrolytes, so the classical Arrhenius theory is still very important.

Possibly strongly ionized electrolytes in solution should be represented



reserving the equilibrium sign for weaker electrolytes in solution.

Solvent Effect of Polar Liquids. The ions already existing in a crystal space lattice are attracted by the polar molecules of water (or similar polar liquids) with such effectiveness that they are actually dispersed or dissolved in the water as shown by Fig. 85. The atmosphere of water molecules around each ion (hydration-of-ion effect) tends to keep these ions separated.

Summary. 1. Acids, bases, and salts are the only substances that, in aqueous solution, conduct electricity with resulting decomposition. Solid metals conduct without decomposition.

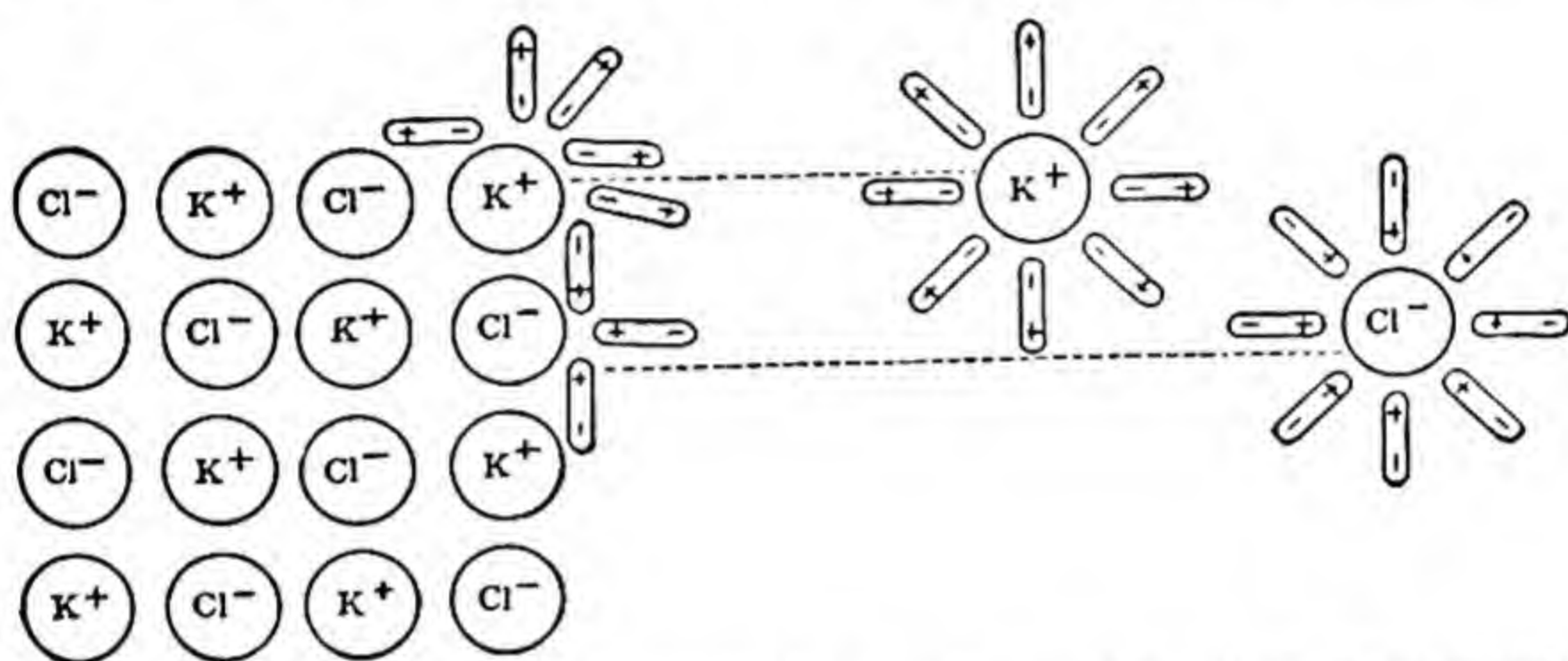


Fig. 85. Solution of solid KCl to form hydrated ions. (After J. H. Hildebrand.)

2. Acids, bases, and salts are the only substances that exchange radicals as in double decomposition, and these same radicals are electrically altered in aqueous solution by electrolysis.

3. Acids, bases, and salts lower the freezing point, raise the boiling point, and produce osmotic pressure in water to an extent not accounted for by a molecular formula. The abnormality of these values is paralleled quantitatively by the electrical conductivity of such solutions. Therefore all, or a fraction, of these molecules must be dissociated into additional particles, which produce the abnormal values.

4. Electrolysis does not cause ionization. It is merely an attraction of radicals to charged plates and their discharge at these plates.

5. The cations (positive charges) are attracted to the negative plate or cathode and there discharged, while the anions are attracted to the positive anode and discharged. The discharged

radicals either are released as primary products of electrolysis or react with the water to form secondary products.

6. By Faraday's law equal quantities of electricity liberate equivalent quantities of the ions. A gram-equivalent weight of any ionic element or radical carries 96,500 coulombs of electricity and therefore this amount is required to discharge and liberate it.

7. The number of positive and negative charges on the ions from each conventional molecule is equal, as shown by the fact that electrolyte solutions as a whole show no trace of electrification. The number of charges on an ion is the same as its valence number.

8. The source of the charges on the ions is the transfer of electrons (negative charges of about $\frac{1}{1837}$ the mass of the hydrogen atom) from the metallic radicals to the non-metallic ones at the time of formation of acid, base, or salt.

Exercises

1. Explain how a metal spoon is silver plated.
2. How many coulombs of electricity are required to decompose 600 g. of copper sulfate, $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$?
3. The number of charges on the ion exactly parallels the valence number. The valence of the phosphate radical (PO_4) is three. How many faradays are required to discharge its weight in grams?
4. If ammonium chloride, when vaporized, completely dissociates into ammonia and hydrogen chloride, what will 22.4 liters of this vapor weigh under standard conditions?
5. Give a convincing array of evidence for the Arrhenius ionic theory.
6. Distinguish between the copper atom and the copper (cupric) ion.
7. State Faraday's laws and give an illustration.
8. What does the electroneutrality of solutions of acids, bases, and salts prove?
9. A toluene solution of HCl gas does not conduct electricity. Would you expect it to attack zinc or marble (CaCO_3) as does a water solution of HCl?
10. Thirty-five g. of sodium nitrate are dissolved in 1000 g. of water. The apparent degree of ionization of the salt in the solution is 70 per cent. What is the freezing point?
11. The same current is passed through separate solutions of each of the following compounds: AgNO_3 , $\text{Cd}(\text{NO}_3)_2$, ZnSO_4 , FeCl_3 . Calculate the relative weights of each of the metals present that are liberated.

12. Suppose that, in the preceding problem, 1800 coulombs of electricity were passed through each solution. Calculate the actual weight of each metal liberated.
13. What weight of iron would be required to displace from solution the copper in 145 g. of CuSO_4 ? See chapter "Electrochemistry."
14. State the evidence for the more modern theory of complete ionization. Its limitations?

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Chapter 21 IONIC REACTIONS

Conductivity and Ionization. The ability of a solution to conduct electricity (its conductivity) depends upon the concentration of ions present, the number of electric charges carried by each, and the velocity of ionic migration and the restriction on movement due to interionic attraction and the resistance (viscosity) of the solution. There is a striking parallel between the conductivity, freezing-point lowering, and chemical activity of normal solutions of acetic, sulfuric, and hydrochloric acids. As Cady states it, under similar conditions (surface, temperature, etc.) normal acetic acid releases 1 ml. of hydrogen when in contact with zinc in exactly the same time that zinc discharges 65 ml. of hydrogen from normal sulfuric acid and 100 ml. from normal hydrochloric acid. Under these conditions hydrochloric acid is one hundred times as active as acetic. A normal solution of hydrochloric acid freezes at nearly twice 1.86° below zero, while a normal solution of acetic acid freezes at only a trifle below -1.86° . Normal acetic acid has but little more effect on freezing-point lowering than has the corresponding concentration of sugar. Normal hydrochloric acid conducts electricity well, sulfuric acid about two-thirds as well, while normal acetic acid is only a very poor conductor.

The conclusion from these facts is that hydrochloric acid in normal solution ionizes completely or nearly so, while in normal acetic acid a very small fraction of the molecules have dissociated.

At greater dilutions even acetic acid ionizes to a greater degree.

In a battery jar (Fig. 86) place two long metal strips as electrodes and fill the jar three-fourths full with water. With a long-stemmed dropping funnel introduce concentrated acetic acid under the lighter water so that there is almost no mixing. After placing a lamp in the circuit turn on the current. The lamp scarcely glows. Now stir the solutions, thus greatly diluting the acid. The bright glowing of the lamp shows the formation of many more ions (with great freedom of movement) at the greater dilutions. It is only ions that conduct in solutions.

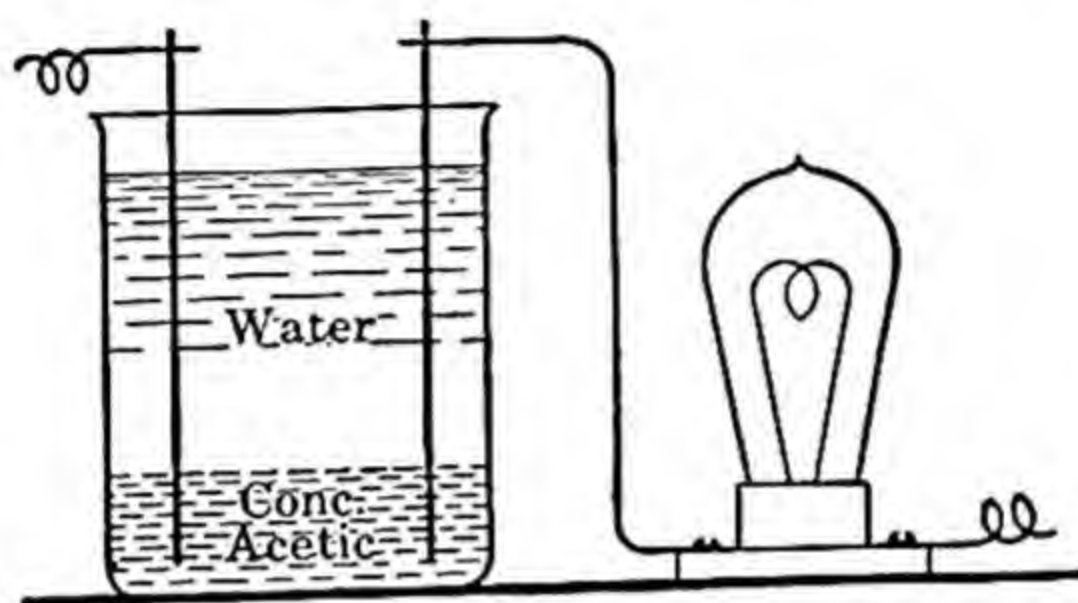


Fig. 86. Increase of conductance with dilution.

Apparent Fraction Ionized. Knowing that strong electrolytes are 100 per cent ionized in dilute water solution it is puzzling to read of 92 per cent ionization of a strong acid. This is readily understood by reference to the crystal lattice of solid sodium chloride. Here each ion is surrounded by six others of opposite charge and each of them is, in turn, surrounded and attracted by six others of opposite charge. It is no wonder there is no mobility to these ions and that the crystal is a non-conductor.

When such a crystalline solid is dissolved (due to attractive forces of the water molecules for ions) there is still, in concentrated solutions at least, a noticeable restriction on freedom of movement due to attraction between ions of opposite charge. The closer these ions are together the nearer is the approximation to the condition in the solid sodium chloride.

In Solid (NaCl),	In Conc. Sol.	In Dil. Sol.
Zero mobility	Moderate mobility	Greater mobility
of ions	of ions	of ions

At any concentration the *apparent fraction* of the molecules ionized may be learned by comparison of the actual conductivity with that calculated on the basis of complete ionization. For

example, if the actual conductivity of a 0.1 N solution of "AB" is 90 per cent of the value calculated on the basis of complete ionization, it is evident that only 90 per cent of the molecules of AB are effectively ionized (at that concentration and temperature).

A table giving the percentage of effective ionization of several acids, bases, and salts is invaluable as a picture of their relative activity:

APPARENT FRACTION IONIZED IN 0.1 N SOLUTIONS AT 18°

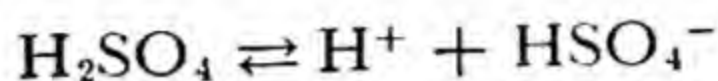
ACIDS		BASES	
HCl	0.92	KOH	0.91
HBr	N/2 .90	NaOH	.91
HNO ₃	.92	Ba(OH) ₂	.77
H ₂ SO ₄ → H ⁺ + H ⁺ + SO ₄ ⁻	.61	NH ₄ OH	.013
H·C ₂ H ₃ O ₂ , Acetic	.0134	N(CH ₃) ₄ OH N/16	.96
H ₂ CO ₃ → H ⁺ + HCO ₃ ⁻	.0017	H ₂ O	.000,000,1
H ₂ S → H ⁺ + HS ⁻	.0007		
HCN, Prussic	.0001		
H·H ₂ BO ₃ , Boric	.0001		
H ₂ O	.000,000,1		
H ₃ PO ₄ → H ⁺ + H ₂ PO ₄ ⁻	.27		
SALTS			
KCl	.86	K ₂ SO ₄	0.72
NaCl	.84	MgSO ₄	.45
NH ₄ Cl	.85	ZnSO ₄	.41
BaCl ₂	.76	CuSO ₄	.40
CaCl ₂	.76	NaC ₂ H ₃ O ₂	.79
KBr	.86	Cd(NO ₃) ₂	.56
NaNO ₃	.83	CdBr ₂	N .16
KNO ₃	.82	HgCl ₂	N .01
Sr(NO ₃) ₂	.72	Hg(CN) ₂	A trace
AgNO ₃	.81		

Salts, with very few exceptions, are "strong electrolytes," or highly ionized in dilute solution. The cadmium halides and some mercuric salts are almost in a separate class.

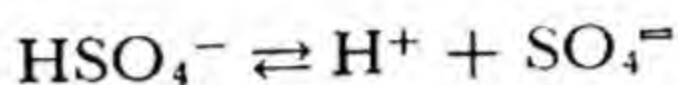
Exercise

1. Classify the electrolytes above in three groups as strongly, moderately, and weakly ionized.

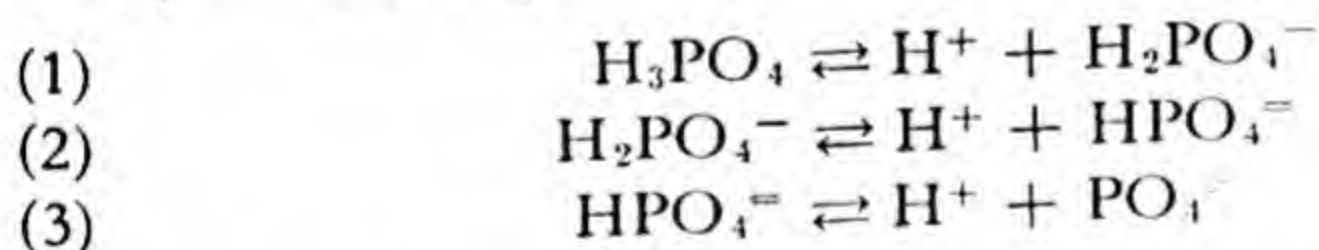
Acids containing more than one ionizable hydrogen atom to the molecule, such as sulfuric, carbonic, or phosphoric, ionize by stages with increasing dilution. With a certain amount of water a given weight of sulfuric acid may first ionize thus:



Addition of more water makes it possible for the second hydrogen to ionize. The algebraic balance of positive and negative charges is still correct:

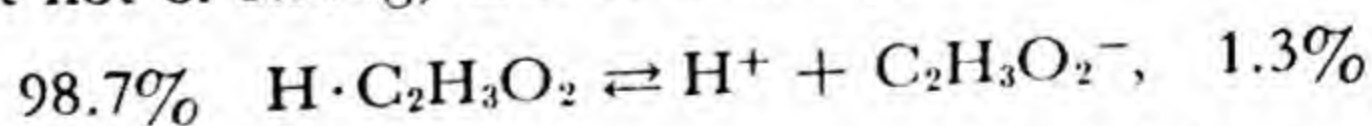


Actually the H^+ ion from the first step represses the weaker second-step ionization. In 0.1 molar solution the concentration of $\text{SO}_4^{=}$ ions is about 0.01 molar. Only 10 per cent of the HSO_4^- ions are dissociated into H^+ and $\text{SO}_4^{=}$ ions; yet in a similar solution of NaHSO_4 about 30 per cent of the HSO_4^- is dissociated. With carbonic acid (H_2CO_3) there is very little of the first, and almost none of the second hydrogen ionized. Phosphoric acid (H_3PO_4) throws off the first hydrogen easily, the second to a very limited degree, and the third almost not at all:



The primary ionization (equation 1) of H_3PO_4 is about 50,000 times the secondary, and this in turn about 500,000 times the tertiary. The first step with H_2SO_4 is 33 times the second.

There is a possibility of some confusion as to the amount of ionizable hydrogen in 0.1 N solutions of a strong acid and of a weak acid. Hydrochloric acid attacks zinc about one hundred times as fast as does acetic, but if the acetic acid is given time enough the same weights of hydrogen will be released by equal volumes of the 0.1 N acids. The reason is that ionization (of weak acid but not of strong) is a case of equilibrium:



If zinc displaces these hydrogen ions from solution, the equilibrium is continuously disturbed to the right (there can be no re-

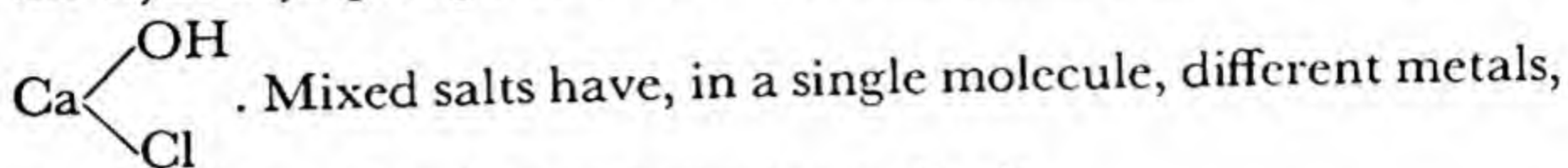
versing to the left with hydrogen ions gone) and finally all the acetic acid molecules have ionized. Thus equal volumes of the same normality of all acids contain exactly equal weights of actual plus "potential" hydrogen ions, but the strong acids contain much more of "actual" hydrogen ions at any instant than do the weaker acids. See Appendix for an explanation of the "pH" system of representing actual hydrogen ion concentration.

Types of Electrolytes. It is now clear that an *acid* is any substance that, in water solution, yields hydrogen ions by direct ionization. In fact it is a proton (H^+) donor. So it is hydrogen ion, common to all acids, that is responsible for the sour taste, the attack on bases and carbonates, and the reddening of litmus. Monobasic acids yield only one hydrogen ion per molecule, as HCl , HNO_3 , $H \cdot C_2H_3O_2$, and HCN . Dibasic (or diprotic) acids yield two hydrogen ions per molecule, as H_2SO_4 . Obviously H_3PO_4 is a tribasic acid. From the formula of acetic acid ($C_2H_4O_2$) it might be thought that four hydrogen atoms should ionize. Only one breaks off as an ion even at great dilutions. The other three are attached differently inside the molecule and are not even potential ions. So we often write the formula $H \cdot C_2H_3O_2$ or even $H \cdot \text{Acetate}$ or $H \cdot OAc$.

A *base* is any substance that yields hydroxyl ions in water solution by direct ionization. A base is also a proton acceptor, as will be shown on page 232. A monoacid base yields but one hydroxyl ion per molecule, as KOH , $NaOH$, and NH_4OH . But $Ca(OH)_2$ is a diacid base and $Al(OH)_3$ a triacid base. We admit that it is only in neutralization that all three hydroxyl groups of $Al(OH)_3$ could be made to ionize, but they are potential ions. **Salts** we defined previously as one of the products of the neutralization of an acid by a base, the other being water.

Salts are substances yielding in water solution cations other than hydrogen ion and anions other than hydroxyl ion. With this interpretation $NaCl$, $CuSO_4$, and Na_3PO_4 are salts, with the understanding that in solid salts the ions are the units in the crystal lattice arrangement. *Normal salts* are formed by replacing all the ionizable hydrogen of an acid by a metal, as in Na_2SO_4 or K_3PO_4 . *Acid salts* are formed by replacing only part of the ioniza-

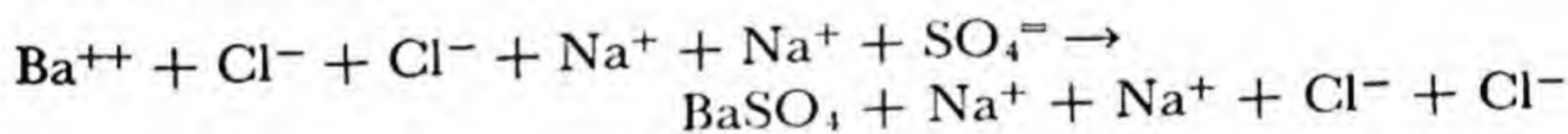
ble hydrogen of acids by a metal, as in KHSO_4 or Na_2HPO_4 , but some of them, notably NaHCO_3 , do not readily yield the remaining hydrogen atom as an ion. **Basic salts** result when only part of the hydroxyl groups of a base are neutralized by an acid, as in



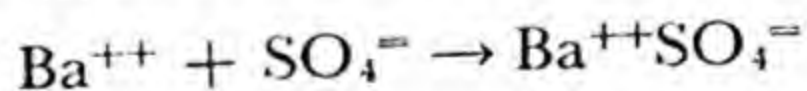
as NaKSO_4 , or different negative radicals.

The positive ion is nearly always a metal, with a few such exceptions as hydrogen and the ammonium ion (NH_4^+). The negative ion never contains a metal alone, but may have it in a radical, as MnO_4^- .

Of course we can form any salt by the simple device of mixing the appropriate oppositely charged ions. For example, to form barium sulfate we need only take a solution of *any barium salt* (because these will furnish Ba^{++}) and mix it with *any soluble sulfate* (because these furnish $\text{SO}_4^{=}$). It is a matter of comparative indifference what the other ions accompanying these are. Mix BaCl_2 and Na_2SO_4 . Solutions of these are already ionized, so we mix four kinds of ions:



The student at once asks why BaSO_4 was written as a molecule on the right. It is so insoluble that it precipitates, leaving the ions of sodium chloride in solution. So the effect is practically this:

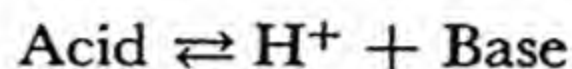


Were barium sulfate soluble we should have only its ions in solution in equilibrium with the others and on evaporating we should have a mixture of four salts.

Upon precipitation of a salt the ions merely enter into the space lattice of the visible solid, not forming molecules in a strict sense. It is however extremely convenient to refer to the substance Na_2SO_4 , for example, as if its smallest unit, with properties characteristic of the mass, had such a composition. Usually in writing equations chemists understand Na_2SO_4 just as clearly as

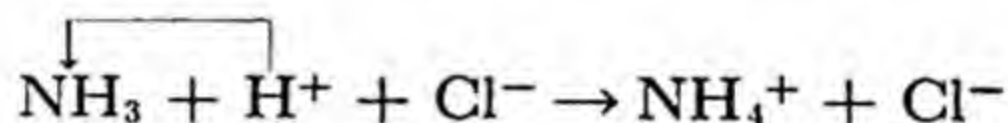
$\text{Na}_2^+\text{SO}_4^-$. The *conventional molecule* of sodium sulfate and of other electrolytes is still very useful.

Broader Concept of Acids and Bases. According to the modern proton-transfer concept of acids and bases, an acid is a substance that yields protons, and a base is a substance that unites with protons. In other words, an acid is a proton donor and a base is a proton acceptor:

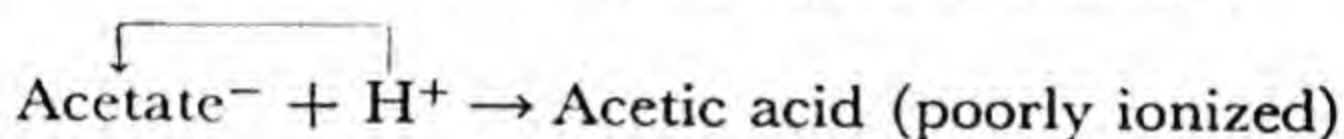
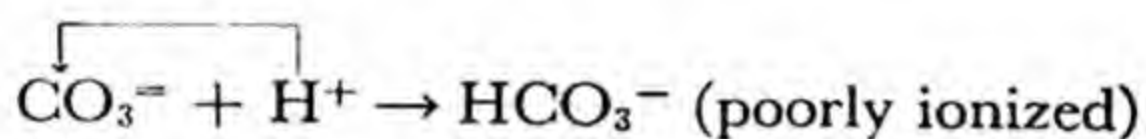


The base may be an ion such as OH^- or S^- or a neutral molecule like NH_3 .

Ammonia, NH_3 , is basic because it accepts a proton (hydrogen ion):



To be consistent we must agree that negative ions are bases when they accept protons:



These are "anion bases" as compared to such "basic hydroxides" as NaOH , KOH , etc. Many writers represent the H^+ ion in water as hydrated, H_3O^+ or $\text{H}_2\text{O} \cdot \text{H}^+$, and call it "hydronium ion." This is cumbersome and should be understood rather than written. We do not trouble to tell the truth about the blue cupric ion, $\text{Cu}(\text{H}_2\text{O})_4^{++}$ as it exists in aqueous solution, every time we write it in an equation.

This section becomes especially important if the instructor elects to omit the next chapter.

Colors of Solutions. Water solutions of sodium chloride are colorless at every concentration, so we conclude that sodium ion and chloride ion, as well as the molecules of sodium chloride, are colorless. The sulfate ion must be colorless because sulfuric acid solutions have no color. Hydrated copper ion must be blue since dilute solutions of copper sulfate are blue. It may be objected that

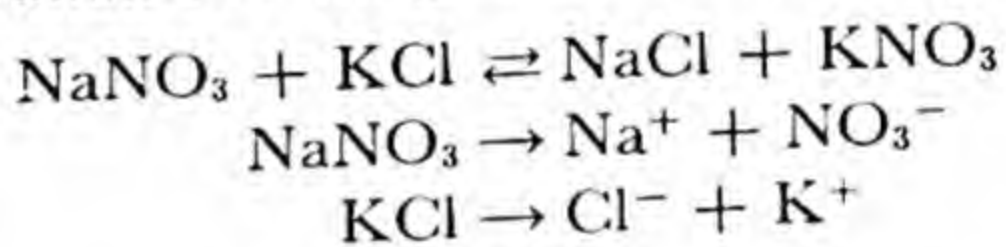
the blue color is due to molecules. This cannot be true, however, because the dry salt, heated until all water is lost, is white, yet only practical molecules or ion pairs remain. In some solutions each ion and the molecules as well may have color. The actual color then is the resultant of a mixture of colors.

2. To what is the color of a yellow solution of potassium chromate (K_2CrO_4) due? The purple of potassium permanganate (KMnO_4) in dilute solution?

Ion Reactions. There are four types of double decomposition:

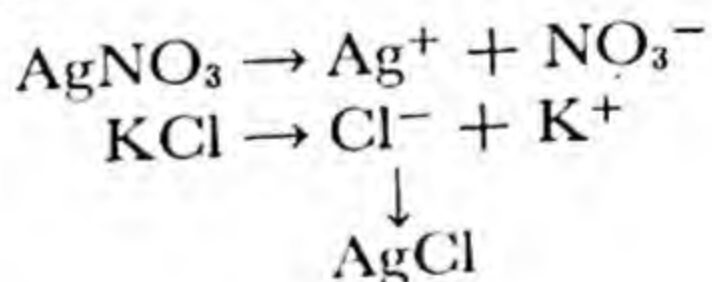
1. Double decomposition with both products soluble
2. Double decomposition with one product insoluble (or slightly soluble)
3. Double decomposition with both products insoluble
4. Double decomposition with one product only slightly ionized.

As an illustration of 1 we give the usual formulation:

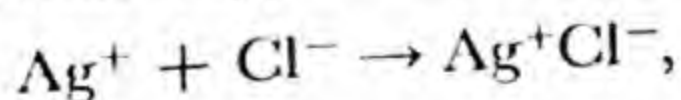


Actually in dilute solution we have only the four ions. Upon evaporation to dryness we bring these ions close together in the crystal lattices of four types of practical molecules.

Type 2 is illustrated by a mixture of solutions of silver nitrate and potassium chloride:



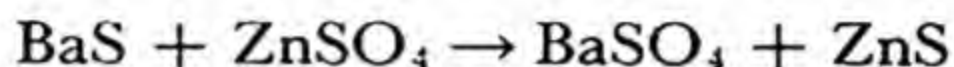
Apparently all that happens is



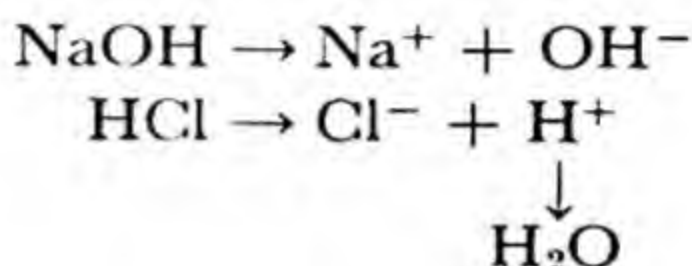
but it is often a practical matter to remember that on evaporating the water from the filtrate a very real substance, potassium nitrate, KNO_3 , is obtained. It is often tedious to tell the whole truth in writing equations.

Since silver chloride is but slightly soluble both the silver ions and the chloride ions are largely removed from solution and tied up in the precipitated silver chloride.

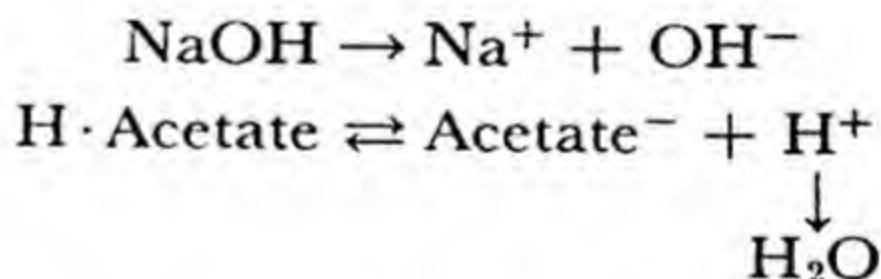
Type 3 is not so common. It is illustrated by the reaction between solutions of barium sulfide and zinc sulfate. All the ions concerned are nearly completely removed in the two insoluble products, barium sulfate and zinc sulfide:



Type 4 is well represented by the neutralization of an acid by a base. Here the hydroxyl and hydrogen ions are tied up in molecules of water, which ionize to only a trifling extent:

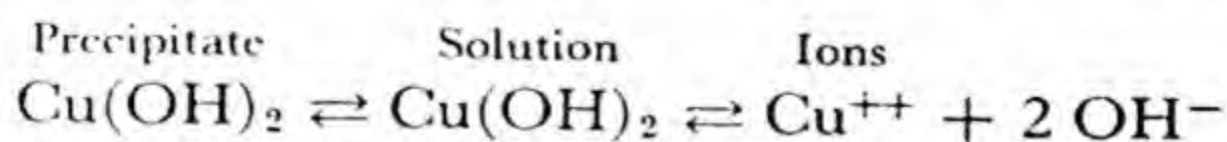


An important variation of type 4 in approximate accord with the classical Arrhenius theory of ionic equilibria should also be represented here:



Here the ionization equilibrium of weak acetic acid is actually displaced to the right by removal of H^+ ions as molecules of water. So with all weak electrolytes.

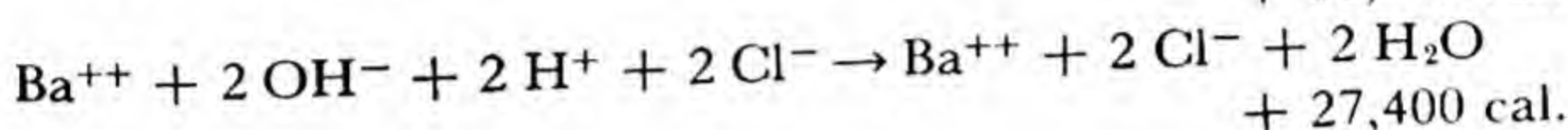
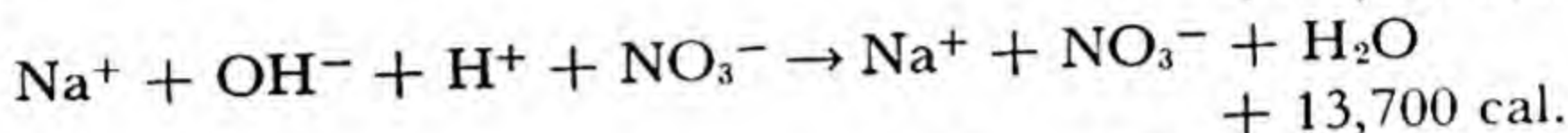
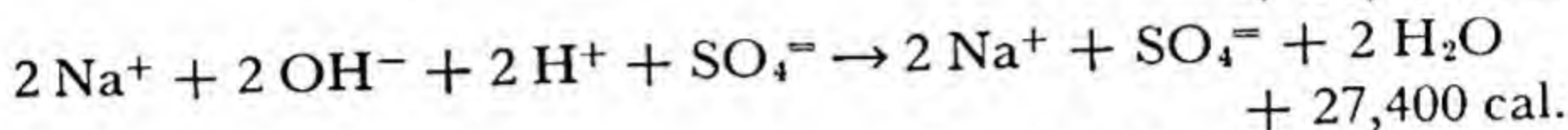
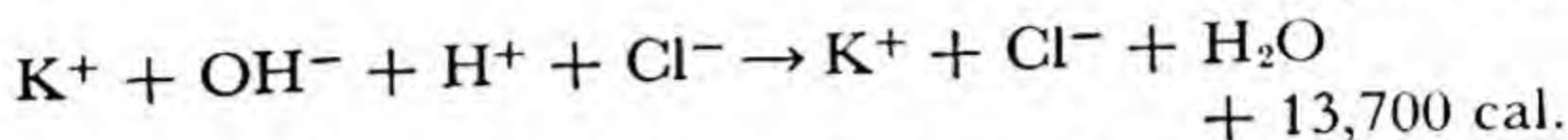
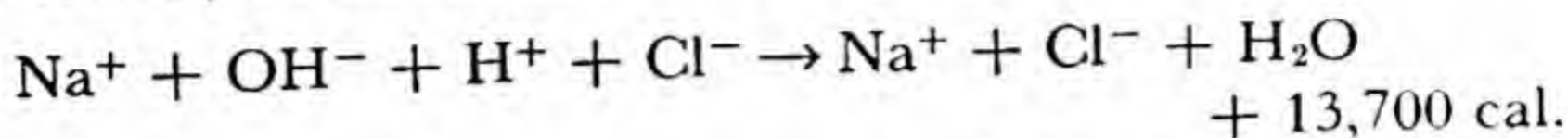
Attack of Acids on Insoluble Hydroxides and Salts. Strictly speaking, the "insoluble" hydroxides and salts actually have a slight solubility and so are in equilibrium with their own ions:



Addition of acids displaces both equilibria to the right.

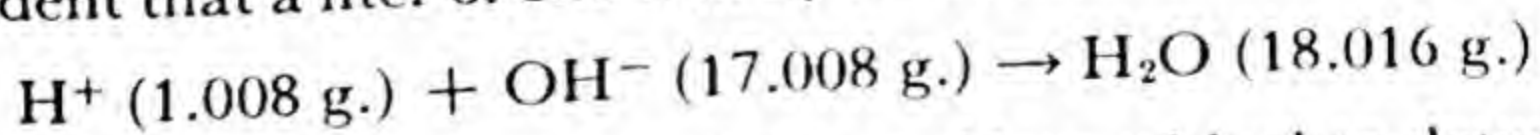
Neutralization. When a liter of a normal solution of *any strong acid* neutralizes a liter of a normal solution of *any strong base* ap-

proximately 13,700 calories of heat are released. Remember, these electrolytes are ionized before they are mixed.



The only thing common to all these reactions is the formation of water. The heat of neutralization is really the heat of formation (from H^+ and OH^-) of 18 g. of water in each case. If sodium chloride really formed and stayed formed in the first reaction above, its heat of formation would be added to 13,700 cal. The same is true for the other salts mentioned, each with a different heat of formation. But the constant value of the heat of neutralization is convincing evidence that the only ions that stay together to any extent are hydrogen and hydroxyl in the form of water. So the essential feature of neutralization is the union of the hydrogen ion of an acid with the hydroxyl ion of a base to form water. Nothing else happens with well-ionized electrolytes.

Titration with Standard Solutions. A solution of any definite, known concentration is often called a *standard solution*. A normal solution of any acid is such a standard solution and contains 1.008 g. of ionizable hydrogen per liter. Since a normal solution of any base contains 17.008 g. of ionizable hydroxyl per liter, it is evident that a liter of one exactly neutralizes a liter of the other:



In fact equal volumes are equivalent. If we wished to determine the strength of an unknown solution of sodium hydroxide (or any base) and had, for example, a 0.1 N solution of hydrochloric acid, we could do this by titration. With an accurately marked

pipette or burette (Fig. 87) we measure out a convenient volume, say 20 ml., of the acid into a small beaker. A few drops of litmus solution are added to this, turning red, of course. Then we carefully run in (drops, not a stream) the unknown base until one more drop just turns the red to blue.

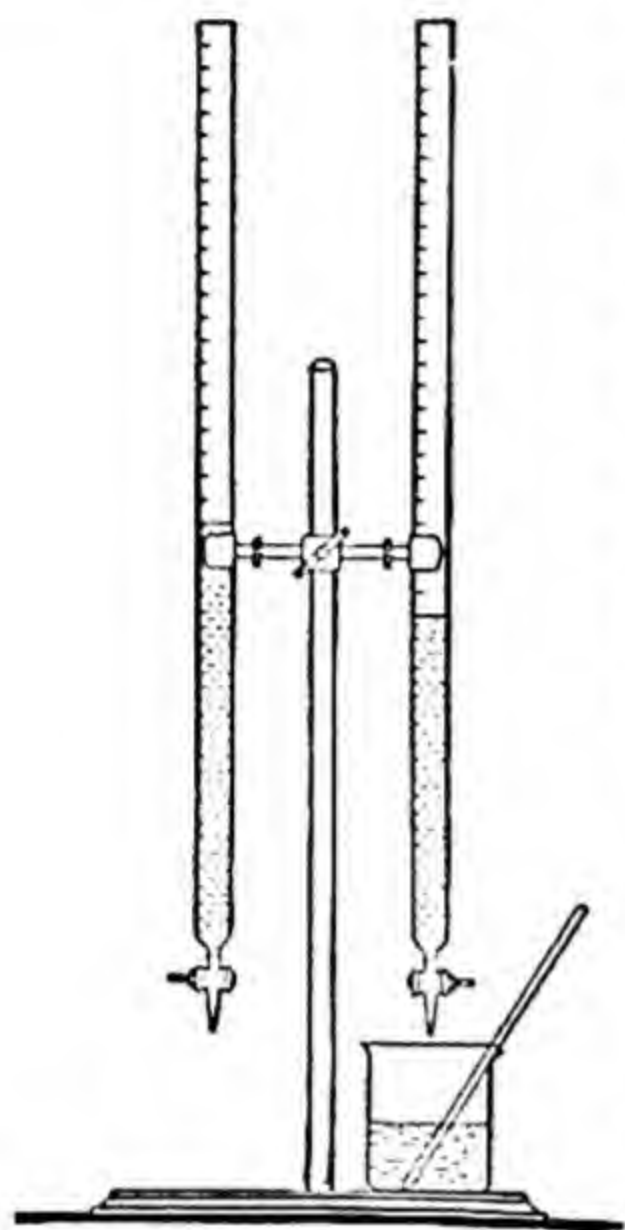


Fig. 87. Titration.

This means that there is just enough base to react exactly with the acid. Suppose 20 ml. of 0.1 N HCl neutralized 16 ml. of unknown sodium hydroxide. It is evident that the volumes of acid and base used must be inversely proportional to their normality. For example, 100 ml. of N acid would neutralize 50 ml. of 2 N base. In this particular case the proportion may be expressed as follows:

Ml. Acid	Ml. Base	Normality of Base	Normality of Acid
20	: 16	= x	: 0.1
	16 x	= 2.0	
	x	= 0.125	

Therefore the base is 0.125 N.

If desired, titration problems may be solved in a different way. In the illustration given the number of grams of HCl in 20 ml. of 0.1 N solution could be calculated. Next the number of grams of NaOH required to neutralize this weight of acid could be calculated (equation, etc.). This is, of course, the weight of NaOH actually contained in 16 ml. of the unknown solution, the volume found by the titration experiment to be equivalent to 20 ml. of 0.1 N acid. It is, then, a simple step to compute the weight of NaOH in 1 ml. and in 1 liter.

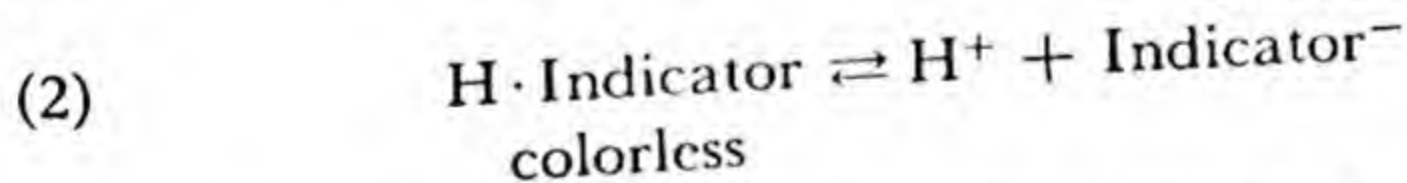
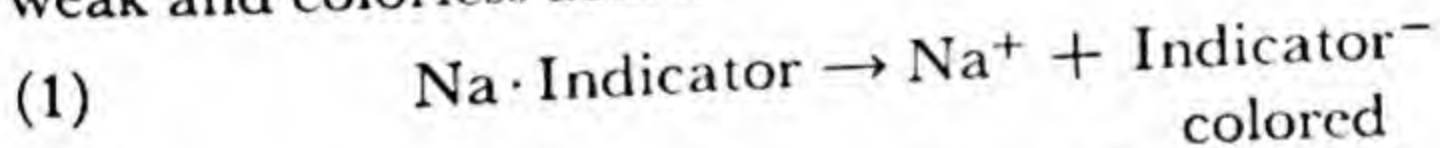
Such analysis of acid or base solutions is called *acidimetry* or *alkalimetry*.

3. How many ml. of 0.1 N HCl are required to neutralize 250 ml. of 1.2 N KOH?
4. If 60 ml. of unknown sulfuric acid neutralize 25 ml. of N KOH, how many grams of acid are contained in 1000 ml.? What is its normality?

5. Remembering that ammonium hydroxide in 0.1 N concentration is only 1.3 per cent ionized, while 0.1 N nitric acid is apparently 93 per cent ionized, would you say that a liter of 0.1 N NH_4OH would just exactly be neutralized by a liter of 0.1 N HNO_3 ? Explain.

Indicators. Indicators are substances that change color when their solutions pass from the acidic to the basic condition or vice versa. The color change at neutrality is called the *end-point* and the process is *titration*. Litmus changes from red in acid to blue in base; phenolphthalein from colorless in acid to pink in base; methyl orange from pink in acid to yellow in base. The sharp color change should indicate neutrality, when the number of H^+ ions exactly equals the number of OH^- ions, but some indicators do not change color until there is a considerable excess of either H^+ ions or OH^- ions. For example, there must be eighty times as many OH^- ions as H^+ ions before phenolphthalein changes to pink. Methyl orange does not become an unmistakable pink until there are a million times as many H^+ ions as OH^- ions. Litmus, in its color change, is closer to the numerical equality of H^+ ions and OH^- ions.

Some indicators, like phenolphthalein, are sodium salts of weak and colorless acids.

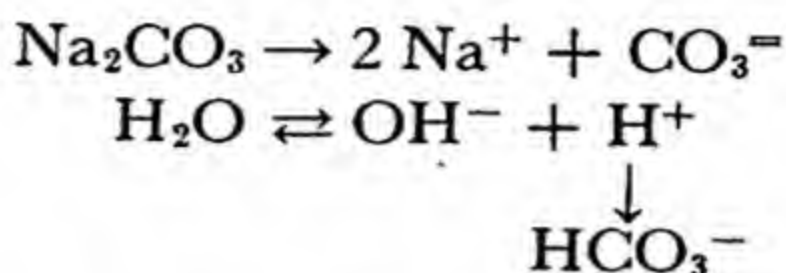


Reaction (2) proceeds but slightly to the right and the solution is colorless until addition of a base, or OH^- ions, displaces the equilibrium to the right, increasing enormously the concentration of the colored "Indicator" ion.

Reaction (1) changes over to reaction (2) upon addition of H^+ ions and the solution becomes colorless.

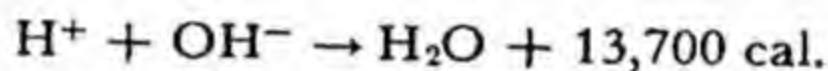
Hydrolysis. Hydrolysis is a reaction between water and some other compound, and depends upon the presence of the ions formed from water. Strictly speaking the term is applied to a reaction of water with a salt, and yet phosphorus tribromide, which is not a salt, is completely decomposed by water. Water

solutions of sodium carbonate are basic. The minute ionization of water (proved by the slight but distinct conductivity of the purest water) is a vital factor.



Only one water molecule out of many millions is ionized, but as the few H^+ ions are tied up in the very weak HCO_3^- ion the further ionization of water is promoted. More water ionizes and the excess of free OH^- ions increases until the solution is very strongly alkaline. The bicarbonate ion, HCO_3^- , is ionized into H^+ ion and $\text{CO}_3^{=}$ ion to such an extremely minute degree that it very effectually removes H^+ ions from the solution.

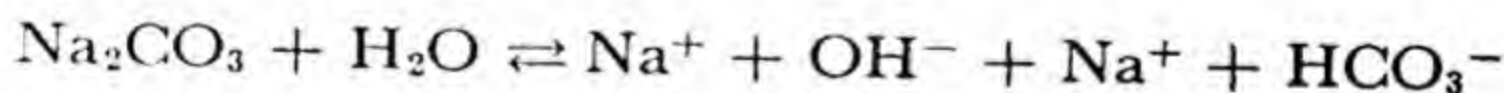
The neutralization of a dilute solution of a strong base with a dilute solution of a strong acid yields the same heat of neutralization in all instances.



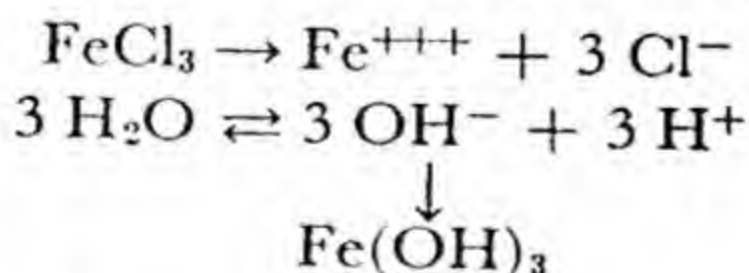
The reverse reaction indicates that heat is absorbed in the ionization of water, therefore, rise in temperature aids this ionization, yielding greater concentration of H^+ and OH^- ions. Hydrolysis of salts increases with rise in temperature.

If a cold, saturated solution of sodium bicarbonate (with phenolphthalein) in a test tube is half immersed in ice water, the cold portion is colorless while the warmer part is colored, due to increased hydrolysis.

The net result of hydrolysis of Na_2CO_3 is an equilibrium condition favored to the right or left by the presence of more or less water:



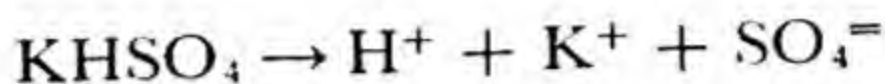
Solutions of ferric chloride react acidic:



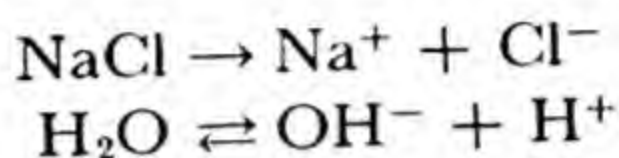
Ferric hydroxide is very insoluble, so it removes OH^- ions from solution and continuously disturbs the ionization equilibrium of

water. Therefore a distinct excess of H^+ ions develops, paired off with Cl^- ions as the equivalent of HCl in solution.

Some salts are acid in solution for a different reason as indicated by:



Solutions of sodium chloride are neutral, as neither H^+ ions nor OH^- ions are removed from solution. The ionization of water is not promoted:

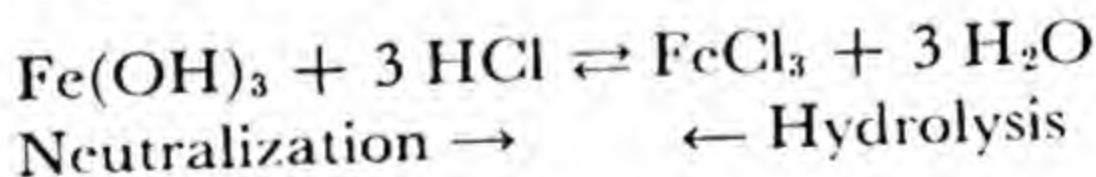


There is, then, no excess of either H^+ ion or OH^- ion.

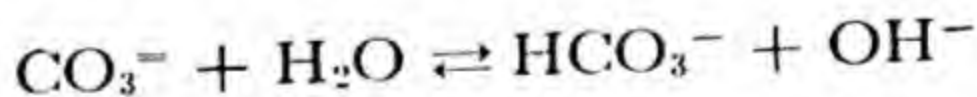
From these type reactions we learn that a salt of a strong base and a weak acid ($2 NaOH + H_2CO_3 \rightarrow Na_2CO_3 + 2 H_2O$) is hydrolyzed to yield a basic solution. Salts of a weak base and a strong acid ($Fe(OH)_3 + 3 HCl \rightarrow FeCl_3 + 3 H_2O$) react acidic in water. Salts of a strong acid and a strong base ($HCl + NaOH \rightarrow NaCl + H_2O$) react neutral in water. Salts of a weak acid and a weak base are nearly completely hydrolyzed.

6. Diagram the hydrolysis of potassium acetate. Of Al_2S_3 .

Hydrolysis is practically the reverse of neutralization:



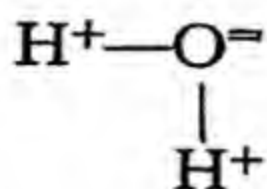
Hydrolysis may be termed the reaction between an ion and water, e.g.



Hydrolysis of a salt evidently depends upon a difference in degree of ionization of the acid and base which had reacted to form that salt. If there is no difference as in $NaCl$ (from $HCl + NaOH$) the solution is neutral.

Influence of Solvent on Ionization. The water molecule is an electric dipole with the center of the positive charge located in

one part of the molecule and the center of the negative charge in another part. It is a two-pole particle somewhat like a magnet:

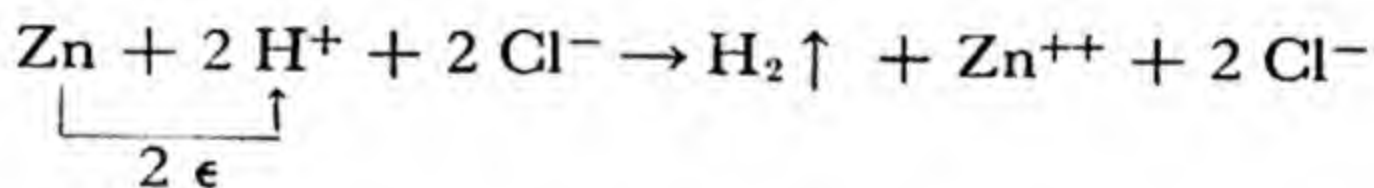


Ions at the surface of a solid electrolyte attract the oppositely charged ends of these dipole water molecules and are pulled away from the solid into solution as hydrated ions.

As it happens the bonds in HCl molecules are not electrovalent, but must be covalent (sharing-of-electrons type) because liquefied dry HCl is not a conductor, unlike fused NaCl which is an electrovalent compound. When HCl is dissolved in water the effect of such a polar solvent is to change the bond to the electrovalent type. Water molecules accept or seize the proton, H^+ , forming the hydrated cation (hydronium ion) and the free chloride ion.

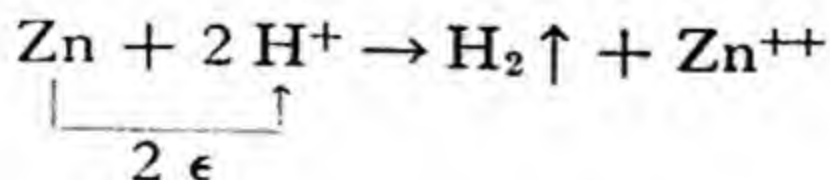
Ionic Displacement. Metals at the top of the activity (or electrochemical) series (see page 99) have the greatest tendency to enter the ionic condition (to lose electrons).

For example:



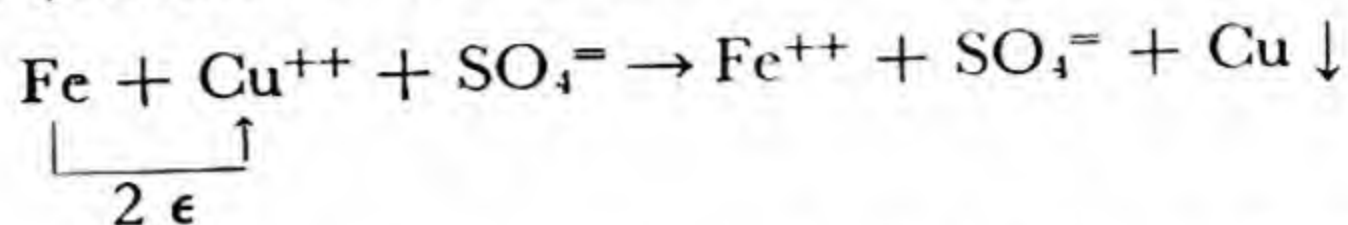
By loss of electrons the neutral zinc atom becomes a positive ion and by gaining those same electrons the positive hydrogen ions become electrically neutral atoms, joining in pairs to form insoluble hydrogen gas.

Since the chloride ions remain unchanged in solution what really happens is:



It is common knowledge that an iron nail dropped into a solution of copper sulfate becomes coated with red copper and that

all the iron eventually dissolves, removing all the blue color from solution (if sufficient iron is used):



From these two experiments and others it is evident that any free metal in the activity series displaces, from solutions of its salts, any metal below it in the series. Metallic zinc gives electrons to ionic hydrogen or to ionic silver, etc. Metallic iron gives electrons (in the same number as its own valence number) to ionic copper but obviously metallic copper cannot give electrons to ionic iron or to the ions of any metal above it.

Exercises

7. What is the result of mixing copper with a solution of zinc sulfate? Explain. Explain the action of iron on a solution of $\text{Pb}(\text{NO}_3)_2$, lead nitrate.
8. Cupric hydroxide, $\text{Cu}(\text{OH})_2$, is a very weak base. Does an aqueous solution of CuSO_4 react acidic or basic?
9. How does hydrolysis prove the ionization of water?
10. If a covalent pair of electrons binding atoms A and B together shifts nearer to the nucleus of A and farther from B, which atom becomes positive and which negative?
11. In aqueous acetic acid solutions there are admittedly both ions and molecules (largely molecules in 0.1 N solution). Upon further dilution more molecules ionize. In terms of covalent and electrovalent linkage of the acidic hydrogen atom to one of the oxygen atoms can you explain the change taking place?
12. What volume of 0.2 N HCl will precipitate all the silver in a solution containing 14 g. of AgNO_3 ?
13. What is the essential difference between the meanings of pH value and normality of an acid solution? (See Appendix.)
14. What types of substances serve as acid-base indicators?
15. Explain why liquid HCl does not conduct electricity.

Chapter 22 THE MODERN THEORY OF ACIDS AND BASES

GENERAL SYSTEMS

In H_2O	$\left\{ \begin{array}{l} \text{Acids yield } \text{H}^+ \\ \text{or } \text{H}_2\text{O} \cdot \text{H}^+ \\ \text{Bases yield } \text{OH}^- \\ \text{Neutralization forms solvent molecules, } \text{H}_2\text{O} \end{array} \right.$ $\begin{array}{l} \text{HCl} \rightleftharpoons \text{H}^+ + \text{Cl}^- \\ \text{KOH} \rightleftharpoons \text{K}^+ + \text{OH}^- \\ \text{KOH} + \text{HCl} \rightarrow \text{H}_2\text{O} + \text{KCl} \end{array}$
In NH_3	$\left\{ \begin{array}{l} \text{Acids yield } \text{H}^+ \text{ which may associate with } \text{NH}_3 \text{ to form } \\ \text{NH}_4^+ \text{ or } \text{NH}_3 \cdot \text{H}^+ \\ \text{Bases yield } \text{NH}_2^- \\ \text{Neutralization forms solvent molecules, } \text{NH}_3 \end{array} \right.$ $\begin{array}{l} \text{NH}_4\text{Cl} \rightleftharpoons \text{NH}_4^+ + \text{Cl}^- \\ \text{KNH}_2 \rightleftharpoons \text{K}^+ + \text{NH}_2^- \\ \text{KNH}_2 + \text{NH}_4\text{Cl} \rightarrow 2 \text{NH}_3 + \text{KCl} \end{array}$
In COCl_2 (phosgene)	$\left\{ \begin{array}{l} \text{Acids yield } \text{CO}^{++} \\ \text{Bases yield } \text{Cl}_2^{--} \\ \text{Neutralization forms solvent molecules, } \text{COCl}_2 \end{array} \right.$ $\begin{array}{l} \text{CO} \cdot \text{Al}_2\text{Cl}_3 \rightleftharpoons \text{CO}^{++} + \text{Al}_2\text{Cl}_3^- \\ \text{CaCl}_2 \rightleftharpoons \text{Ca}^{++} + \text{Cl}_2^{--} \\ \text{COAl}_2\text{Cl}_3 + \text{CaCl}_2 \rightarrow \text{CaAl}_2\text{Cl}_3 + \text{COCl}_2 \\ \text{acid} \qquad \qquad \text{base} \qquad \qquad \text{salt} \qquad \qquad \text{solvent} \end{array}$
Pure solvents ionize slightly	$\left\{ \begin{array}{l} \text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^- \\ \text{NH}_3 \rightleftharpoons \text{H}^+ + \text{NH}_2^- \\ \text{COCl}_2 \rightleftharpoons \text{CO}^{++} + \text{Cl}_2^{--} \end{array} \right.$

It is interesting to note that, although anhydrous liquid phosgene, COCl_2 , is a very poor conductor of electricity, a solution of anhydrous AlCl_3 in phosgene attacks metals, metallic oxides, carbonates, and conducts electricity 100,000 times as well as the pure solvent. Furthermore when such a solution is electrolyzed carbon monoxide escapes at the cathode and chlorine at the anode, an action reminiscent of the electrolysis of a dilute aqueous solution of sulfuric acid. Metals displace hydrogen from

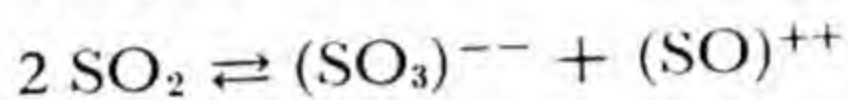
aqueous acid solutions but from substances which are acids in phosgene only carbon monoxide gas may be displaced. Salts with phosgene of crystallization are known just as, in aqueous systems, salts with water of crystallization are prepared.

Ammonium nitrate in liquefied ammonia attacks steel and some metals as well as their oxides and hydroxides, acting like an acid in water.

Exercise

1. If KSH were considered as a base in the liquid H_2S system what would be an acid? How would neutralization operate?

Liquefied sulfur dioxide is also an ionizing medium, itself dissociating to some extent as follows:



The $(\text{SO})^{++}$ cation is comparable to H^+ in the water system while the $(\text{SO}_3)^{--}$ anion compares to OH^- in water.

2. How would dissolved SOCl_2 act in SO_2 ? And what role would K_2SO_3 play? Explain and complete $\text{K}_2\text{SO}_3 + \text{SOCl}_2 \rightarrow ?$

Our theories of solution and ionization have developed largely from a study of water solutions. Yet we have long known that fused salts are excellent solvents for other salts and that they ionize and may be electrolyzed.

Franklin and others called attention to the solution, ionization, neutralization, and electrolysis possible in liquefied ammonia (NH_3 , not NH_4OH) as decidedly parallel to similar phenomena in the usual water system. Others have shown similar parallels in liquefied hydrogen sulfide, hydrogen cyanide, sulfur dioxide, phosgene, etc.

NOTE: Since first-year college chemistry deals mainly with water as solvent for electrolytes it is not obligatory at this stage to apply the modern Brönsted theory. It is offered here to broaden the student's conceptions of chemistry although it may be applied from now on if desired.

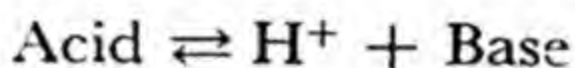
This theory is not universal for no protons are involved in acid-base reactions in phosgene (COCl_2) or in high-temperature reaction between a basic oxide such as CaO with SiO_2 . Other exceptions might be named.

From the comparisons above, it might be stated that acids in general are ionic compounds which in any solvent yield the same cation as the solvent does while bases are ionic compounds that yield the same anion as the solvent. Neutralization is the formation of solvent molecules from appropriate cations and anions leaving a salt, or its equivalent ions, in solution or as a precipitate.

THE BRÖNSTED THEORY

Brönsted (aided by earlier work of others) in 1923 proposed a simple but universal system of acids, bases, and salts. His definition of an acid can not be applied to the phosgene system.

An acid is a substance that yields protons, and a base is a substance that unites with protons. In other words, an acid is a proton donor and a base is a proton acceptor.



Any molecule with an unshared pair of electrons can act as an acceptor for a proton.

The base may be an ion such as OH^- or S^{2-} or a neutral molecule like NH_3 . In special instances the relations may be formulated as follows:

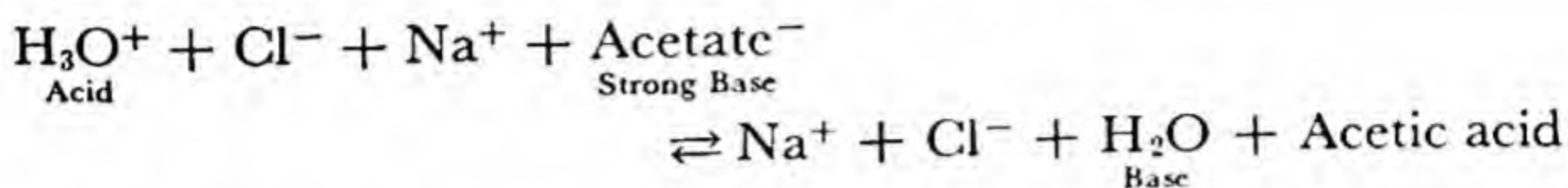


The acids and bases bearing this relation are called corresponding or **conjugate** acids and bases.

It is very doubtful if protons, relatively minute in size and greatly outnumbered by the water molecules of an aqueous solution of acid, can exist free. Brönsted and his followers prefer to speak of the proton, or hydrogen ion, in aqueous solution as definitely associated with a solvent molecule. Not the hydrogen ion H^+ , but the "hydronium" ion, $\text{H}_2\text{O} \cdot \text{H}^+$ or H_3O^+ (sometimes called the "oxonium" ion), is the characteristic of all aqueous solutions of acids. And, since the H_2O molecule unites with a proton, water acts in this instance as a base, according to the Brönsted definitions.

For that matter, negative ions are bases when they accept protons. In water solution the chloride ion has but little tendency

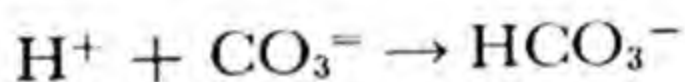
to unite with protons. But the acetate ion is quite competent to decrease the acidity of dilute aqueous solutions of HCl by uniting with hydrogen ions (rather, hydronium ions) to form poorly ionized molecules of acetic acid. Note what happens when sodium acetate is added to dilute hydrochloric acid.



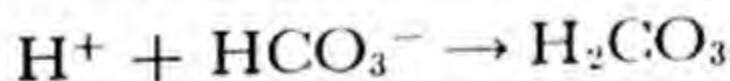
Here the acetate ion may be called the "conjugate base" to the hydrogen ion.

"Basic substance" is a useful term. "Basic hydroxides" applies to hydroxides of the metals. The most important property of bases is their ability to neutralize acids, but other substances than hydroxyl ions can do this.

The $\text{CO}_3^{=}$ ions are basic in the sense that they unite with hydrogen ions or protons.



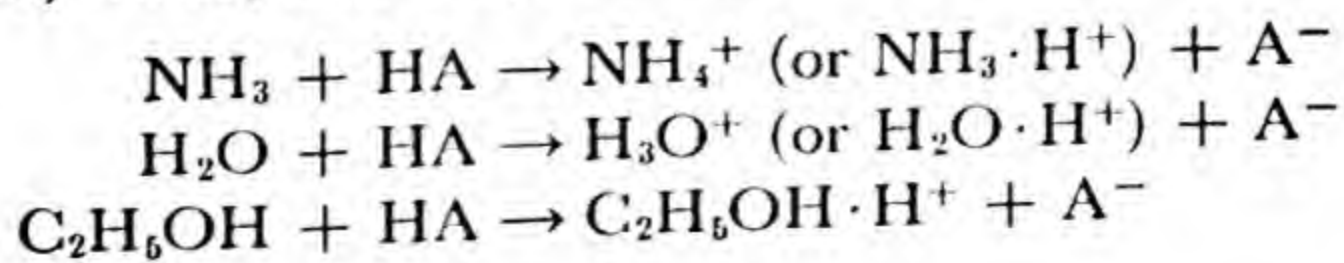
The HCO_3^- ions are also basic but less so.



An X-ray photograph of crystalline $\text{HClO}_4 \cdot \text{H}_2\text{O}$ shows that the ClO_4^- ion is one unit in the space lattice and that the other is not the H^+ ion but a hydrogen ion (or proton) closely associated with a water molecule as H_3O^+ or $\text{H}_2\text{O} \cdot \text{H}^+$.

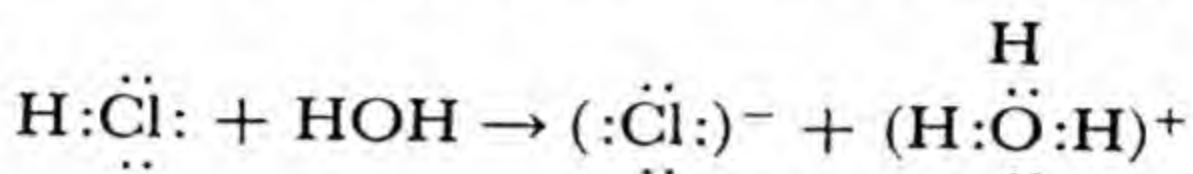
All negative ions, being proton acceptors to some degree, are considered to be bases with a special distinction given to OH^- as the strongest base which can exist in water solution.

Apparently the process of ionization in a solvent is dependent upon a close association of molecules of the solvent with the ions formed. In an acid solution the proton is attached by covalence to a molecule of the solvent. Compare solutions of acids in liquid ammonia, water, and ethyl alcohol.



Substitute HCl for the general acid term, HA, above and you have well-known reactions. Even the alcohol molecule as solvent can hold a proton, taking on its positive charge for the entire unit, $C_2H_5OH \cdot H^+$.

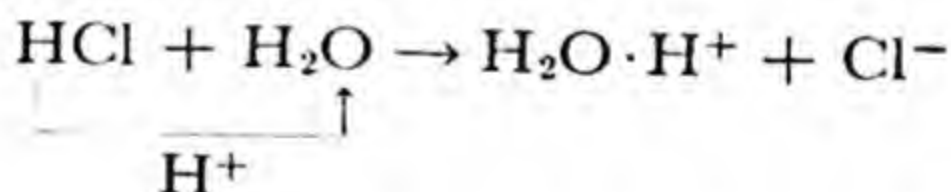
When HCl gas is dissolved in water the strong attraction of water for the proton tears it away from the chlorine atom, leaving to chlorine the electron originally contributed by the hydrogen atom in forming a pair of electrons shared with chlorine.



Briefly, $HCl + H_2O \rightarrow Cl^- + H_2O \cdot H^+$. From $H:\ddot{S}:H$ water can draw away only a few protons or hydrogen ions. Consequently H_2S is but slightly ionized in water.

Anions of unit charge and large radius hold protons weakly because they cannot approach closely enough to the proton to attract it firmly. With greater charge the attraction increases and the acid is weaker as in H_2S .

Certain covalent chlorides such as HCl and $AlCl_3$ react with water to form ionic compounds.



Protons, or H^+ ions, have a great tendency to unite with OH^- , HS^- , HCO_3^- , and other anions of very weak acids but most ions do not unite in solution to form actual molecules. However, ion pairs may exist briefly.

When acids dissolve in non-ionizing solvents they yield no H^+ ions, yet they may show color changes with indicators as they react with basic substances.

3. What ion is the base in a water solution of Na_2CO_3 ? In KSH solution?

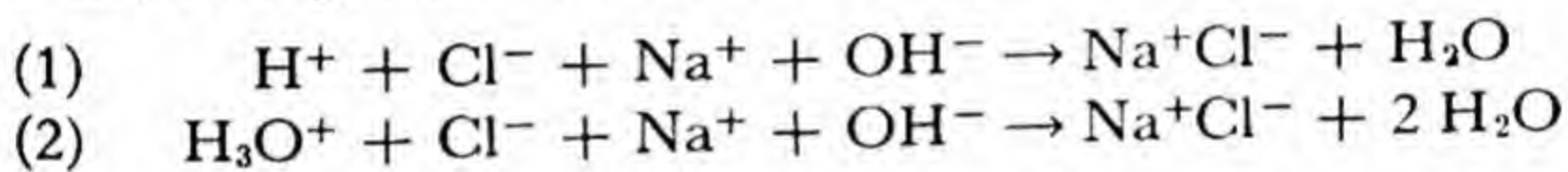
If the H_2O molecule were a stronger proton acceptor it could break the bond by which the H^+ ion is held to one of the oxygen atoms of acetic acid, $CH_3 \cdot COOH$, and thus promote "ionization." Strong bases (such as the OH^- ion) can do this.

In some instances the dielectric constant (insulating capacity of solvent) has only a secondary influence on ionization. Hydrogen chloride dissolved in ethyl alcohol, $\text{C}_2\text{H}_5\text{OH}$, is a strong acid while dissolved in nitrobenzene, $\text{C}_6\text{H}_5\text{NO}_2$, it is a weak acid. The dielectric constants are nearly the same. The explanation is that $\text{C}_2\text{H}_5\text{OH}$ readily accepts protons, H^+ ions, while $\text{C}_6\text{H}_5\text{NO}_2$ is a poor proton acceptor.

The Brönsted theory does not change our conception of the titration of acid-base in water but does force upon us a new viewpoint in titrations in non-aqueous solutions.

Acids in such solvents do not contain or liberate protons (as in water) but other cations instead.

It certainly is unnecessarily cumbersome to write H_3O^+ instead of H^+ in equations which are supposed, by their shorthand character, to represent action and thought at their simplest.



In (2) there is an extra molecule of water to remember and in many other equations different from neutralization the H_2O part of H_3O^+ must be carefully disentangled and accounted for on the right. Possibly no harm is done if one remembers that the proton (hydrogen ion) is hydrated as H_3O^+ and then proceeds to write down the simplest possible symbol for it, H^+ . There is good precedent here for it is the general practice to ignore hydration of other ions, $\text{Cu}(\text{H}_2\text{O})_x^{++}$, etc., in writing equations.

Exercises

4. Why is H_2S so weakly ionized in water solution?
5. How is it possible that covalent AlCl_3 when dissolved in water conducts electricity so well?
6. Why isn't HCl ionized when dissolved in benzene?
7. Why is the acetate ion a good base and the chloride ion a poor one?

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Chapter 23 EQUILIBRIUM

We have had illustrations of reversible reactions or processes arriving at equilibrium on pages 96 and 135. Others will appear.

Exercises

1. Give an illustration showing how an ionic equilibrium can be disturbed by tying up one of the ions in molecules of a weak acid or a weak base.
2. The preparation of a pure compound by double decomposition depends upon a choice of reacting ions such that the reaction shall proceed to completion or nearly so. Give examples of different ways in which this may be done.

Two types of equilibria are shown in Fig. 88, a reaction equilibrium and a solution equilibrium. If the bottle is only partly filled, NH_3 escapes into the air space until the velocity of return of NH_3 molecules equals that of escape, when an equilibrium results. If the stopper is removed, NH_3 molecules wander away without adequate return, thus disturbing the solution equilibrium. The loss of more dissolved NH_3 disturbs the reaction equilibrium and finally nothing but water is left in the bottle.

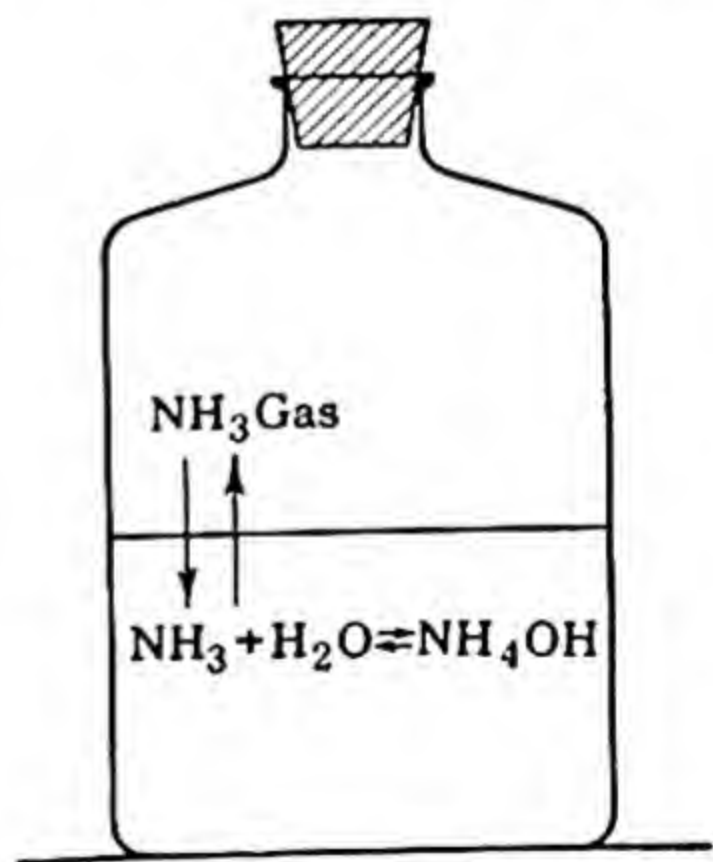
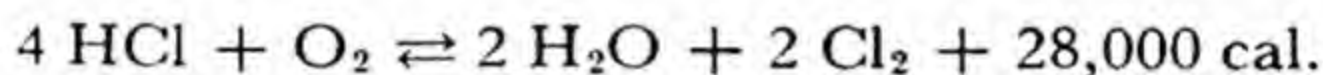


Fig. 88. Two types of equilibria.

3. What would happen if to a bottle half filled with ammonia water an excess of acid were added, the stopper quickly replaced, and the bottle shaken?
4. Iodine water is shaken with carbon disulfide. Then a base is added with shaking. Explain why the carbon disulfide becomes colorless.

Effect of Change in Temperature. All reactions increase in speed with rise in temperature, but such increase is not the same in all cases. Thus one reaction in an equilibrium condition may be accelerated more than the opposing reaction. As a result the equilibrium would be disturbed and a new adjustment of reaction velocities reached. That reaction will be favored which absorbs heat. "With rise in temperature an equilibrium is disturbed in the direction which absorbs heat" (Van't Hoff's Law). For example, Deacon's obsolete process of making chlorine from hydrogen chloride works best at a moderate temperature:



A rise in temperature disturbs the existing equilibrium to the left.

Of course some heating is necessary to secure sufficient velocity of reaction.

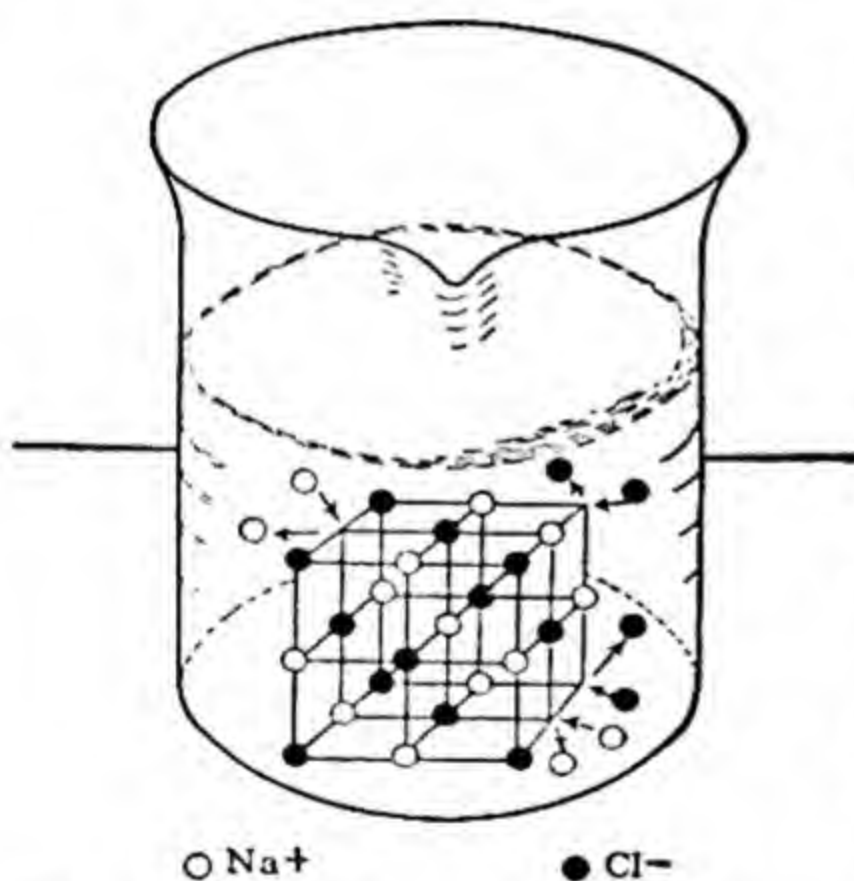
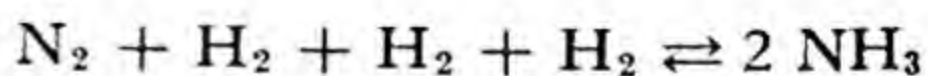


Fig. 89. The solution equilibrium of the system, sodium chloride crystal in water, involves only the movement of ions from the space lattice into solution and back into the space-lattice pattern.

Effect of Change in Pressure.

Any increase in pressure on a system in equilibrium tends to bring reacting particles in closer contact and to compress the products. Consequently the formation of substances occupying a smaller volume will be favored. For example, one volume of nitrogen reacts with three volumes of hydrogen to form only two volumes of ammonia:



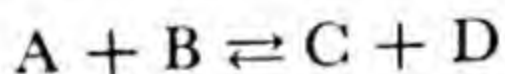
In Haber's process great pressure is applied because pressure favors the formation of two volumes of ammonia from a total of four volumes of nitrogen and hydro-

gen. It goes without saying that high pressure must oppose the expansion involved in the decomposition of ammonia into its elements. This is an application of the Principle of Le Chatelier:

"When a stress is applied to a system in equilibrium that reaction is favored which tends to undo the stress."

Effect of a Catalyst. The effect of a catalyst is merely to bring about an increased velocity of reaction and thereby hasten the approach to equilibrium. This is commercially important, for some opposing reactions do not come to a definite equilibrium for months unless hurried by a catalyst. If a catalyst could really disturb an existing equilibrium, it would be possible to get work done without any expenditure of energy by alternately removing and putting back the catalyst — a scientific impossibility.

The Law of Mass Action. The speed of a reaction is proportional to the molecular concentration of the reacting substances and is also influenced by the nature of the molecules involved. (By a concentration of "1" we mean one gram-molecular weight per liter.) With solids and homogeneous liquids such concentration changes with variations in pressure are not to be expected as with gases and substances in solution. Consider a reaction between two gases, A and B, to yield C and D:



Suppose we have, in a unit volume, just 1,000,000 molecules of A and an equal number of B. At a given temperature, etc., the speed of reaction to the right will be definite. But if we double the concentration of A, use 2,000,000 molecules per unit volume without changing B, it is obvious that the speed of reaction will be doubled because there will be just twice as many contacts per second between A and B as before. If we then treble the concentration of B, take 3,000,000 molecules per unit volume, the previous speed of reaction must be trebled, due to three times as many contacts per second as before. The final speed must be six times the original speed since it was once doubled and that speed immediately trebled.

The same facts may be expressed in another way. Let the molecular concentration of A (number of gram-molecular weights per liter) be represented by $[A]$ and the molecular concentration of B by $[B]$. Since the velocity of reaction is proportional to the concentration of A and also to that of B, it must be proportional to their product:

$$[A] \times [B] \propto \text{speed}$$

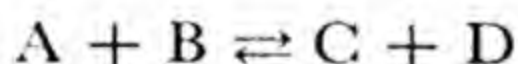
Now it isn't really true that the number represented by this product equals the number of gram-molecular weights of C and D formed per second (the speed). We merely mean to say that the speed changes proportionately to any change in this product of the concentrations of A and B. We should, however, be justified in introducing a factor peculiar to the reaction, letting it represent all the other influences affecting a reaction. $[A] \times [B]$ represents the concentration influence only, but we must remember that temperature, affinity, and catalysis have an effect. Combine all but the concentration influence in k , which remains constant during any changes in concentration:

$$[A] \times [B] \times k = \text{speed}$$

The speed of reaction between hydrogen and iodine is represented in exactly the same way:

$$[H_2] \times [I_2] \times k = \text{speed}$$

Application to an Equilibrium Reaction. Let us assume that the reaction discussed is reversible:



Without further discussion it is evident that the speed of reaction to the left is proportional to the molecular concentrations of C and D, and to a constant factor k' peculiar to that reaction:

$$\text{speed} = [C] \times [D] \times k'$$

When equilibrium is reached the two speeds are equal:

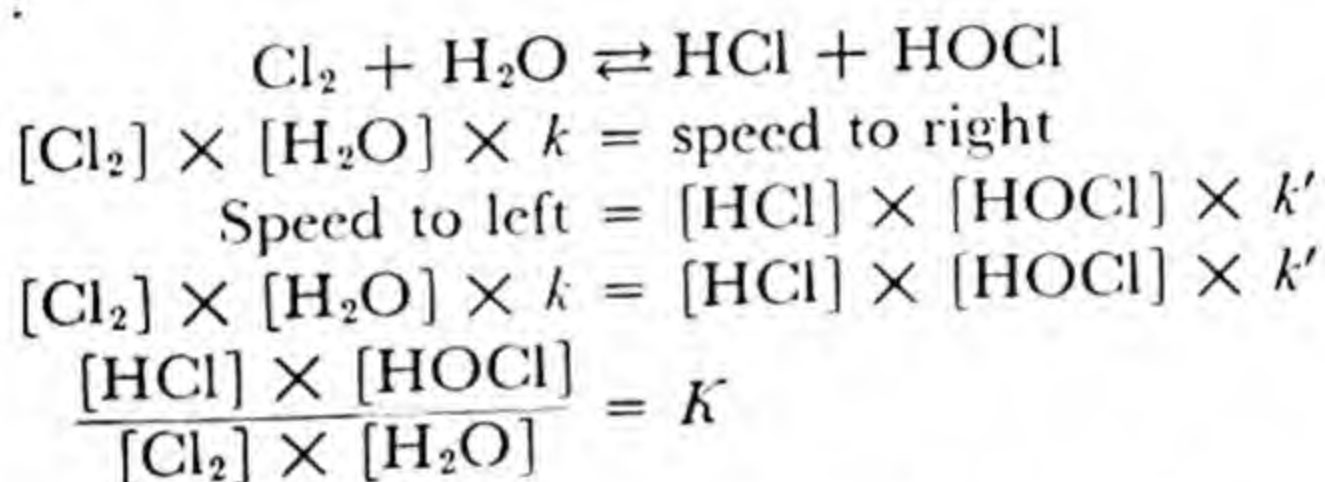
$$[A] \times [B] \times k = [C] \times [D] \times k'$$

By a simple algebraic process we may transform this into a more useful statement:

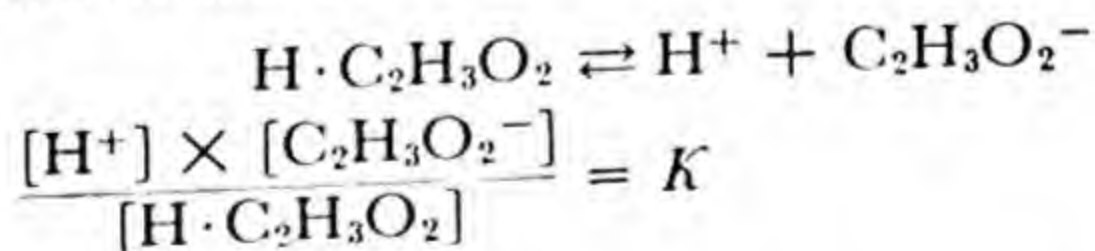
$$\frac{[C] \times [D]}{[A] \times [B]} = \frac{k}{k'} = K$$

Since both k and k' were constant factors, despite the changes in concentration the quotient $\frac{k}{k'}$ must also be a constant value represented by K . The convenient phrase "equilibrium constant" is applied to K .

An illustration of the application of the equilibrium constant may be found in the conditions present in a solution of chlorine in water:



Applications to Ionic Equilibrium. It is very interesting to formulate and compare equilibrium constants for weak acids and bases. Here we begin to see some reason for the preceding derivation. In the case of ions a molecular concentration of "1" means the "molecular" weight of the ion in grams per liter. Since the acetate ion weighs 59, there should be 59 grams of this ion per liter to give a molecular concentration of 1. Consider a typical weak acid, such as acetic:



Acetic acid is also written, $\text{H} \cdot \text{OAc}$.

In a 0.1 N solution of acetic acid it is known (from electric conductivity measurements, etc.) that 98.68 per cent of the molecules are, at any instant, undissociated while 1.32 per cent have ionized. Purely as an aid to quick thinking we might argue that if the solution were 1 N instead of 0.1 N and if none of the

molecules ionized the molecular concentration would be exactly 1. Similarly we might argue that in a 0.1 N solution, if none of the molecules ionized, the molecular concentration would be 0.1. But proceeding from fancy to fact we learn that in this 0.1 N solution 98.68 per cent (not 100 per cent) remains in the molecular condition. Consequently the molecular concentration is $0.1 \times 0.9868 = 0.09868$.

By similar reasoning, starting with a tentative hypothesis that ionization is 100 per cent, we learn that the ionic concentrations are $[H^+] = [OAc^-] = 0.1 \times 0.0132 = 0.00132$, since each molecule which dissociates will produce one H^+ and one OAc^- ion. We learned above that the concentration of undissociated molecules $[H \cdot OAc] = 0.09868$.

$$K = \frac{0.00132 \times 0.00132}{0.09868} = 0.0000177 = 1.77 \times 10^{-5}$$

For weaker acids (and bases) the ionization constant is still smaller. For example, for hydrocyanic acid, HCN , $K = 7 \times 10^{-10}$.

Dilution does not change the ionization constant, because of the readjustment of all numerical values in the fraction above.

IONIZATION CONSTANTS 25°

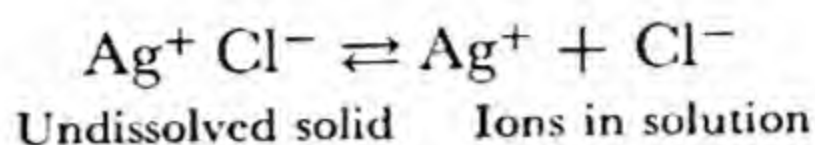
Acetic acid	1.86×10^{-5}	Sulfuric	4×10^{-1}
Carbonic	3×10^{-7}	Sulfuric (2d·H)	1.9×10^{-2}
Carbonic (2d·H)	6×10^{-11}	Ammonium hydroxide	1.8×10^{-5}
Prussic	7×10^{-10}	Water	10^{-14}

In an aqueous solution of ferric chloride the equilibrium, $2 FeCl_3 + 3 H_2O \rightleftharpoons 2 Fe(OH)_3 + 6 HCl$ can be displaced to the left by addition of HCl . This also forces formation of more molecules of $FeCl_3$ from its ions (and excess Cl^- from HCl). Mix water, ether and ferric chloride in a test tube and shake. An upper layer of water (containing some ether) and a lower layer of ether (containing some water) form. Ferric chloride is distributed in both layers, and more will dissolve in the ether if HCl is added. Molecules of this salt are more soluble in ether while its ions are more soluble in water.

Molality of HCl	2.5	4	6	8	10
Per cent of $FeCl_3$ in ether	0.5	40	98	82	2.7

The maximum is at 6 to 6.5 M. HCl

The Solubility Product.¹ An equilibrium between the ions in a saturated solution of silver chloride (slightly soluble) and the ions in the space lattice of a solid fragment in contact with the solution may be formulated as below:



If this were formulated by the classical Arrhenius theory it would appear like this:

$$\frac{[\text{Ag}^+] \times [\text{Cl}^-]}{[\text{Ag}^+\text{Cl}^-]} = K$$

But the concentration of Ag^+Cl^- (molecules to Arrhenius) in a saturated solution could not change as long as saturation continued, so $[\text{Ag}^+\text{Cl}^-]$ may be called a constant:

$$\frac{[\text{Ag}^+] \times [\text{Cl}^-]}{k} = K$$

or

$$[\text{Ag}^+] \times [\text{Cl}^-] = K \times k = K' \text{ in a sat. sol.}$$

Whatever the inaccuracies of deriving this formulation from the Arrhenius theory it is practically correct for the saturated solutions of electrolytes that are only slightly soluble.

In saturated solutions of slightly soluble salts (or electrolytes) the product of the gram-ionic concentrations (solubility product) is a constant.

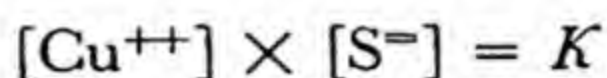
Such solutions are very dilute and interionic attractions almost negligible.

On paper one might attempt to formulate a similar equilibrium, or ionization, constant for strong acids, bases, and salts, but K in any such instance is not really a constant value at different concentrations. No wonder, for such molecules in any but concentrated solutions are practically completely ionized. We may speak of the "apparent degree of ionization" but this simply means that interionic attractions and viscosity interfere so much

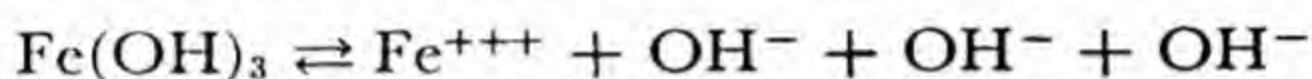
¹ A brief table of solubility products is found in the Appendix.

with freedom of movement of ions that the "effective concentration" of ions may be less than that calculated on the basis of complete ionization. With greater dilution this interionic attraction decreases as the ions are separated farther apart by the solvent.

With a very low concentration of Cu^{++} ions in a solution there need be added only a small concentration of $\text{S}^{=}$ ions to exceed the extremely small solubility product of copper sulfide and thus cause precipitation:

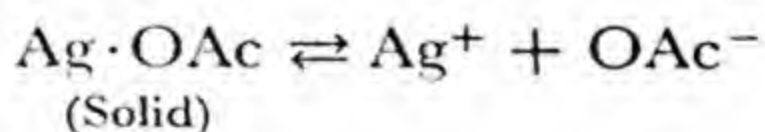


The converse of the above must be that whenever the product of the concentrations of any two ions in a saturated solution is made less than the actual solubility product of this compound, any undissolved substance present must dissolve. If to a suspension of $\text{Fe}(\text{OH})_3$ any acid is added, the precipitate dissolves:



The H^+ ions of the acid unite with OH^- ions to form water. Consequently the product of the concentrations of the Fe^{+++} ions and OH^- ions falls below the solubility product and more precipitate must dissolve.

Effect of a Common Ion. The effect of exceeding the solubility product is well demonstrated by the addition of about 10 ml. of a saturated solution of silver nitrate to 250 ml. of a saturated solution of the slightly soluble silver acetate. The solubility product of the latter at room temperatures is about 4×10^{-3} .



In half a minute or less a precipitate of silver acetate settles out because of the increase in concentration of the silver ion. The same result of the common ion effect may also be shown by addition of about 10 ml. of a saturated solution of sodium acetate to 250 ml. of the silver acetate solution.

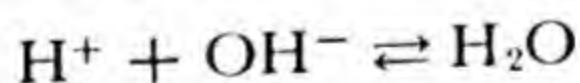
The precipitate may be redissolved by addition of concentrated ammonium hydroxide which reduces the Ag^+ -ion concentration through the formation of a silver-ammonia complex ion.

Acetic acid is a weak acid but more than sufficiently ionized to turn methyl orange red. If to such a red solution a considerable amount of sodium acetate is added, the color changes to yellow, indicating a great suppression of H^+ ion:

$$\frac{[H^+] \times [OAc^-]}{[H \cdot OAc]} = K$$

Sodium acetate, like all soluble salts, ionizes very well, but comparable acetic acid solutions contain a relatively small percentage of ions. Addition of much sodium acetate, therefore, greatly increases the concentration of the acetate ion in the equilibrium for acetic acid. Apparently this must increase the numerical value of the numerator in the above fraction, yet actual laboratory measurements show that K has not changed. The explanation is simple: any increase in the concentration of acetate ions affords more opportunities for contact with hydrogen ions, thus decreasing the concentration of hydrogen ions since some of them are tied up in the molecules of acetic acid thus formed. Suppose the concentration of acetate ions were increased 100 times. We might conclude that the concentration of hydrogen ions must be decreased to one hundredth of its previous value, but the value of $[H \cdot OAc]$ is also increasing. The fact is, all values adjust themselves so as to maintain K as a constant. Addition of potassium acetate would suppress the ionization of acetic acid in the same way.

Equilibrium in Acidic and Basic Solutions. As shown by the facts of hydrolysis there is an equilibrium in pure water:



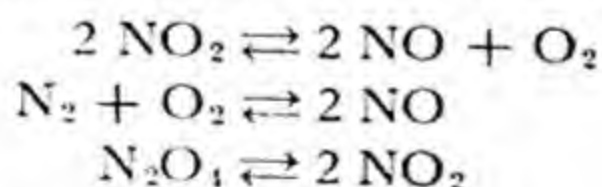
Addition of an acid disturbs this equilibrium to the right and decreases the concentration of OH^- ions, perhaps almost to the vanishing point. Addition of a base to water also disturbs the equilibrium to the right by decreasing the concentration of H^+ ions. In each case it is a matter of addition of a common ion, either H^+ ions or OH^- ions. "Mass action" expresses it. It is usual for us to think of an acid solution as marked by the presence of H^+ ions and entire absence of OH^- ions. Such is not the case.

An acidic solution is merely one in which there are *more* H^+ ions than OH^- ions. A basic solution contains more OH^- ions than H^+ ions. A neutral solution contains H^+ and OH^- in the same concentrations.

Hydrolysis equilibria may be expressed so as to give a "hydrolysis constant" but that subject is more suitable for advanced study.

Exercises

5. What is the effect of adding ammonium chloride to a solution of ammonium hydroxide?
6. Are there any OH^- ions in a solution of an acid?
7. What is the Principle of Le Chatelier? Give an application.
8. What is the equilibrium effect of addition of solid sodium chloride to a saturated solution of silver chloride?
9. In a crystal of calcium carbonate there are Ca^{++} ions and CO_3^{--} ions arranged in a space lattice. Of course this "insoluble substance" really has a slight but measurable solubility. Explain in detail the mechanism of attack by dilute hydrochloric acid on CaCO_3 solid immersed in water.
10. What is Van't Hoff's Law? Give an application.
11. Copper sulfate is very soluble and copper sulfide very insoluble. Which has the larger solubility product?
12. In a molar solution of ammonium hydroxide the apparent fraction ionized is .0047. Calculate the ionization constant.
13. What would happen to the acidity of a solution of hydrochloric acid if much sodium acetate were added? If any sodium salt of a weak acid were added?
14. Which reactions would be favored by increased pressure?



All the substances above are gases.

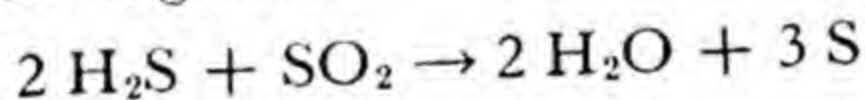
Chapter 24 SULFUR AND HYDROGEN SULFIDE

SULFUR

(Selenium and tellurium are in the sulfur group. They are discussed on page 284.)

Sulfur was known to the ancients. The brimstone of the Bible was sulfur. Later the alchemists considered it one of the three fundamental elements.

Occurrence. Sulfur occurs free in volcanic regions, possibly because of the reaction between sulfur dioxide and hydrogen sulfide found in volcanic gases:



Sedimentary sulfur also occurs in large deposits because of the reduction of calcium sulfate by bituminous material to form calcium sulfide (CaS), the release of hydrogen sulfide by the action of carbonic acid on the calcium sulfide, and final oxidation of the hydrogen sulfide to free sulfur. Combined sulfur is found in several metallic sulfide ores as well as in gypsum ($\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$), barite (BaSO_4), celestite (SrSO_4), and Epsom salt ($\text{MgSO}_4 \cdot 7 \text{H}_2\text{O}$).

Sulfur is an essential element in all protein material and so is found combined in plants and animals; hence the production of the offensive-smelling hydrogen sulfide on decay. Egg protein is so rich in combined sulfur that spoiled eggs are easily recognized by the overpowering odor of hydrogen sulfide.

Preparation. Sulfur volatilizes at very moderate temperatures and thus may be distilled away from its impurities. The vapors are condensed in large brick chambers. At first, before the brick

walls are heated by the gases, the sulfur settles as a yellow dust called "flowers of sulfur." Later it condenses as a liquid which is cast into sticks of "roll sulfur."

In the United States the clever invention of Herman Frasch, an American chemist, made possible the cheapest production of pure sulfur (99.5 per cent) yet known.

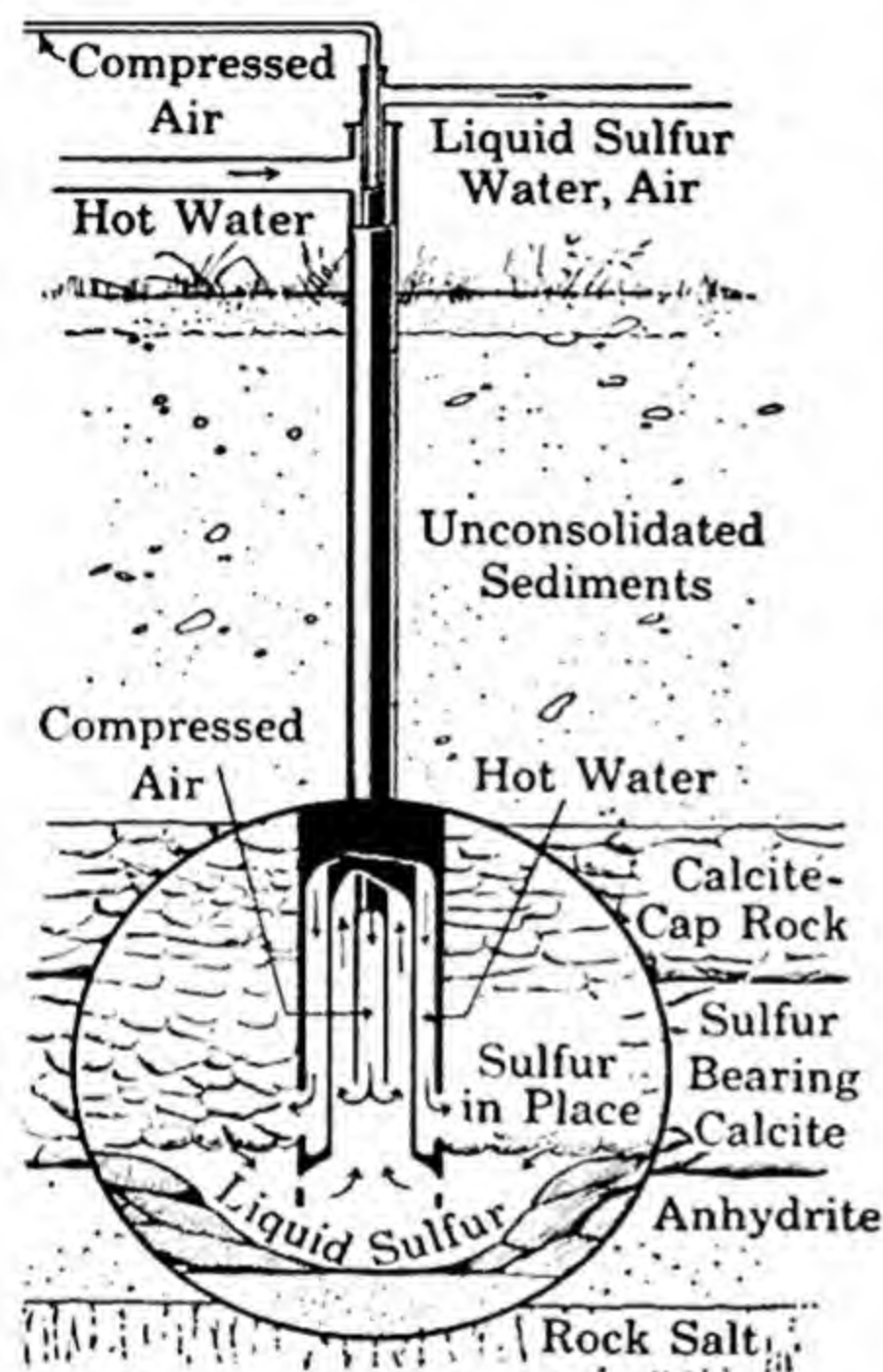


Fig. 90. A sulfur well. (Courtesy *The duPont Magazine*.)

In Louisiana and Texas great beds of sulfur occur at depths approaching 900 ft. A boring through the overlying rock reaches the bottom of these deposits and into this hole three or four concentric pipes are driven (Fig. 90). The outer pipe has a diameter of about 8 in. Relying on the remarkably low melting point of sulfur (112.8°), water at 170° C. under 100 pounds pressure is forced down an outer pipe to melt the sulfur. But sulfur is twice as heavy as water, so to make it lighter, hot air is forced down the innermost pipe (1 in.) to fill the liquid with bubbles. The frothy mixture rises between the air pipe and the hot-water pipe and flows into great wooden bins, where it

cools to huge blocks. Many wells yield 500 tons daily. Some of the bins produce a single block containing several hundred thousand tons of sulfur. The great block, 99.5 per cent pure, is blasted into fragments, as needed for loading on trains. The Louisiana-Texas field produces about 4,000,000 tons of nearly pure sulfur yearly. Sicily is a poor second in annual production.

Germany formerly recovered 50,000 metric tons of sulfur annually from coke-oven gases by controlled oxidation of the hydrogen sulfide.

Physical Properties. Sulfur is a pale-yellow solid, tasteless, and nearly odorless, insoluble in water but soluble in carbon disulfide and some other solvents. It exists in a number of different forms with distinctly different properties. This is an example of *allotropy*. (Ozone and ordinary oxygen are allotropic forms of the same element. White and red phosphorus, as well as diamond and graphite, are also examples of allotropes.) The stable form of sulfur, at ordinary temperatures, crystallizes in the rhombic system, but above 96° it slowly changes into the needle-like monoclinic crystals. On cooling the monoclinic crystals below 96° they change very slowly to rhombic crystals. Thus 96° is a *transition point*.

Exercise

1. In what connection have we mentioned transition points before?

There is a distinct change in properties in this transition. The density of rhombic sulfur is 2.07 and its melting point 112.8° . The density of monoclinic sulfur is 1.96 and its melting point 119° . Of course natural sulfur is rhombic. This form can be obtained in the laboratory by allowing a solution in carbon disulfide to evaporate slowly (away from flames). If a large mass of molten sulfur (about 200 g.) is cooled slowly, the surface crust is punctured, and the liquid below poured out, the dish will be found to contain a mass of needles of monoclinic sulfur. On long standing below 96° these become rhombic. Apparently the needles remain, but upon examination they are found to be made up of minute rhombic crystals.

Amorphous Sulfur. Sulfur boils at 444.6° but shows unusual property changes on heating. When sulfur is melted it first turns into a thin, pale-yellow liquid, easily poured, then shows a rapid increase in viscosity at 159.5° . At 230° the liquid becomes black and very viscous but at higher temperatures the viscosity again decreases. This is due to changing proportions of S_{λ} , S_{μ} , and, possibly, other forms. Alexander Smith called the pale-yellow liquid S_{λ} and the thick dark liquid S_{μ} . He proved that at intermediate temperatures the two forms are in equilibrium, their

relative amounts shifting with the temperature. If sulfur heated nearly to boiling is quickly poured into cold water, it solidifies before crystals have time to form and becomes a rubbery mass. This soon hardens and then is only partly soluble in carbon disulfide. Crystalline S is removed by this solvent, leaving non-crystalline S_{μ} . A trace of iodine acting as a negative catalyst delays the return of amorphous sulfur to the crystalline form. There is only 3.6 per cent S_{μ} at 120° but 34 per cent at 445° .

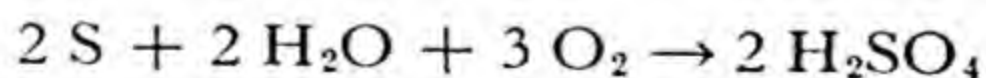
Amorphous S_{μ} is also made by the reaction between sulfur dioxide and hydrogen sulfide, at 0° . (See page 259.) Solutions of polysulfides when acidified yield a suspension of S_{μ} called *milk of sulfur*. The solid removed after slow settling is insoluble in carbon disulfide.

Under 160° the sulfur molecule is probably an eight-membered ring but above 160° the rings are broken into chains that hook up and tangle to produce a great increase in viscosity. Chlorine or a trace of iodine shortens these long chains and thus decreases the viscosity.

Sulfur Vapor. At 230° (under low pressure) sulfur must be represented by S_8 since 22.4 liters, corrected to standard conditions, weigh 256 g.

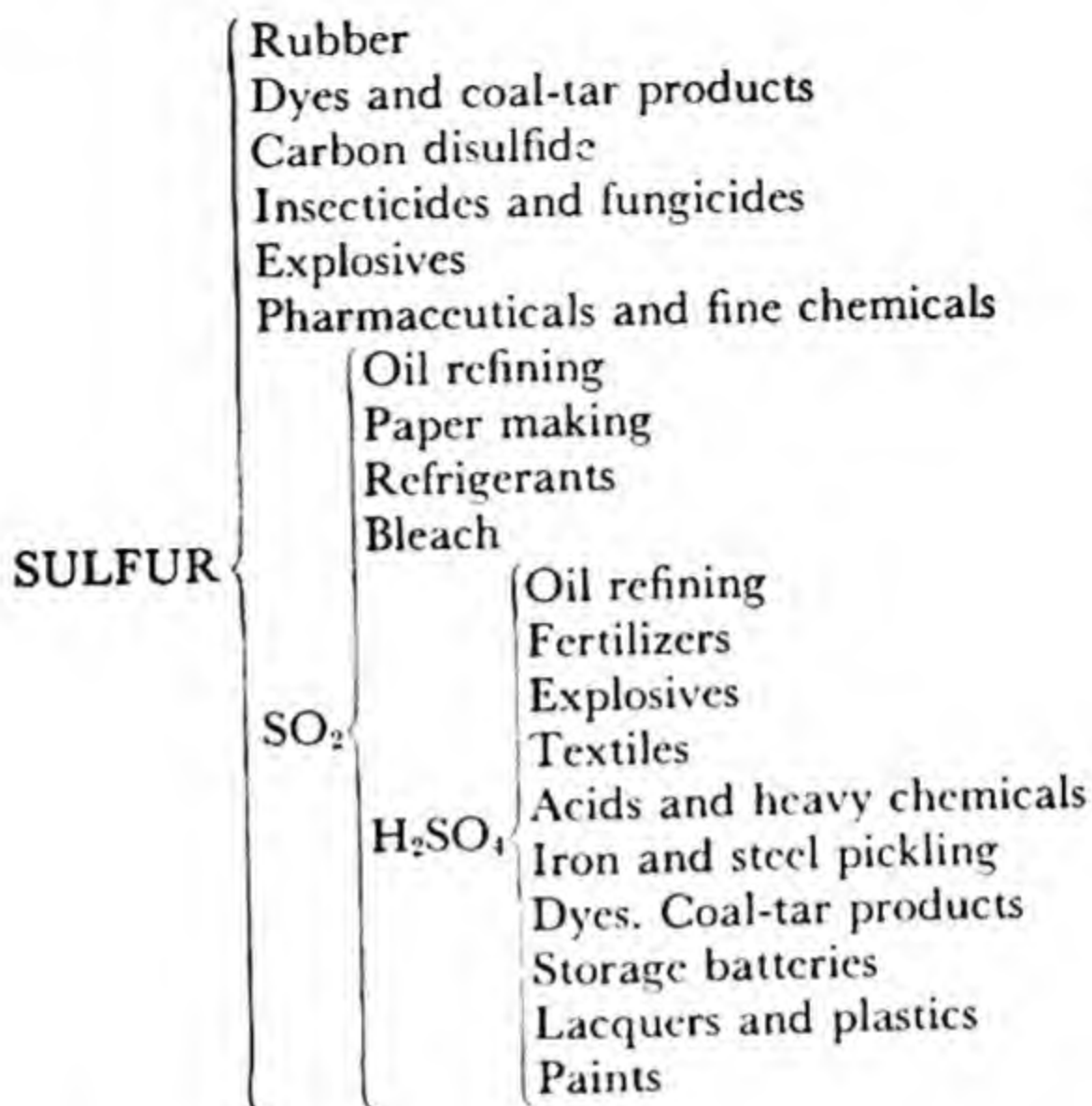
At 800° the G. M. V. weighs 64 g., so S_2 is then the formula. At intermediate temperatures S_6 may exist, but probably there are only mixtures of S_8 and S_2 . In contact with air at such temperatures the hot vapors would burn.

Chemical Properties. Sulfur is very active when heated. Merely rubbing it in a mortar with mercury produces black mercuric sulfide (HgS). When heated it unites with all metals except gold and platinum and, when the reaction once is started, much heat is evolved. If a tube containing sulfur and iron filings is heated to glowing, the glowing continues even after removal of the tube from the flame. Moist sulfur is slowly oxidized in the air:



It can be oxidized quickly by strong oxidizing agents, such as hot nitric acid. In fact sulfur compounds are torn down by this method and the sulfur is converted into sulfuric acid. It may then

be converted into insoluble barium sulfate and weighed. This is the basis of our quantitative determination of sulfur in minerals, and in foods. Of course hot sulfur burns in air to form sulfur dioxide -- and a trace of trioxide.



Hot sulfur unites with carbon to form carbon disulfide, and with hydrogen to form hydrogen sulfide. Sulfur reacts with hot chlorine to form the monochloride, S_2Cl_2 , which at 0° unites with more chlorine to yield the dichloride, SCl_2 . Sulfur monochloride was once thought to be SCl , hence the misleading name. The valence number of sulfur in H_2S is two, in SO_2 four, and in SO_3 six.

More than 40,000 tons of sulfur are used yearly in vulcanizing natural rubber. Sulfur is in demand in the manufacture of carbon disulfide and matches and the sulfur-black dyes. Free sulfur is a necessary part of black gunpowder and of many fungicides and insecticides for plants. Europe annually applies 100,000 tons of the element to grapevines and to hops. The lime-sulfur spray is famous in this country. As sulfur dioxide, sulfur is necessary in the bleaching of straw and some other fabrics and has been in demand for bleaching dried fruits, English walnuts, etc. Solid

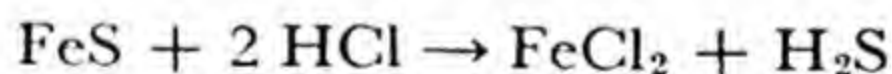
sulfur has a high electric insulating power, resists wetting by water, is inactive towards most acids, and has a fair degree of physical strength. These properties promise the development of new uses. Since moist sulfur corrodes steel it is best transported in aluminum cars.

2. How many grams of sulfur are required to make 55 liters of sulfur dioxide?

HYDROGEN SULFIDE

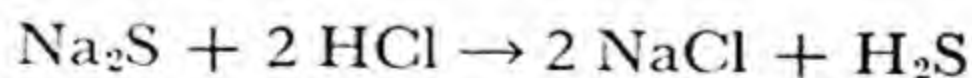
Hydrogen sulfide is found in some natural waters, such as the so-called "sulfur springs," in volcanic gases, and in Mexican oil wells. Since albuminous material contains combined sulfur, its decay in the absence of air produces hydrogen sulfide. Thus sewer gas always contains hydrogen sulfide. In the distillation of soft coal some hydrogen sulfide is formed, necessitating the passage of the coal gas through layers of ferric oxide.

Preparation. Hydrogen unites with hot sulfur vapor to form hydrogen sulfide, and this is a reversible reaction. The most convenient laboratory method of preparation is the addition of some non-oxidizing acid to a suitable sulfide, preferably ferrous sulfide (FeS) because it is very cheap:



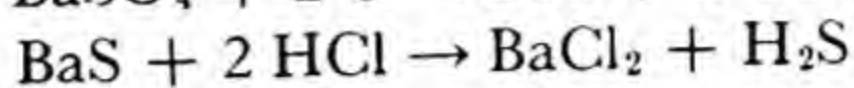
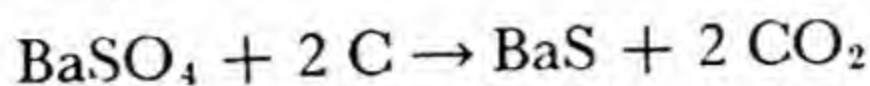
This reaction is slightly reversible but owing to the escape of most of the H_2S it runs practically to completion. It might reasonably be expected that iron pyrites (FeS_2) would be better since it is still cheaper, but it is not used because it does not react with an acid to form hydrogen sulfide, unless "active" atomic hydrogen is present.

Soluble sulfides, such as sodium sulfide, react with acid rapidly (better contact), but for simple regulation of flow as in a Kipp generator the insoluble ferrous sulfide is best:

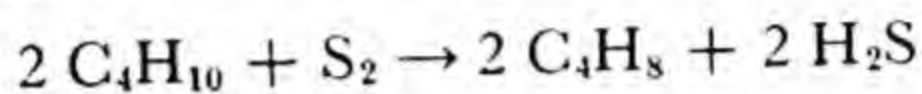


Since hydrogen sulfide is an acid in aqueous solution, the sulfides of metals are its salts. Many occur in nature and many are formed by addition of soluble sulfides to salt solutions. Any sulfate

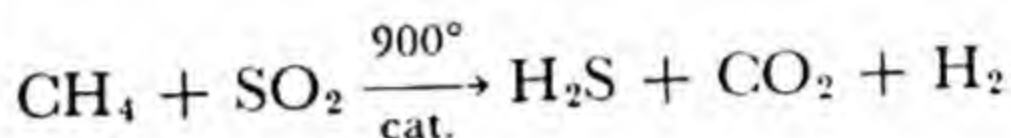
can be reduced to the sulfide by heating with carbon. If hydrogen sulfide is made from the resulting metallic sulfide, the two reactions together may serve as a test for the original sulfate:



Sulfur heated with paraffin (a compound of carbon and hydrogen) is a convenient laboratory source of hydrogen sulfide. With butane the reaction is similar.



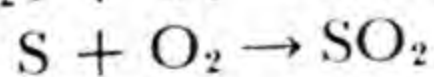
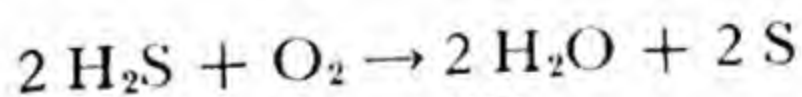
Hydrogen sulfide may also be prepared from the methane of natural gas.



There is an increasing industrial demand for this gas, H_2S .

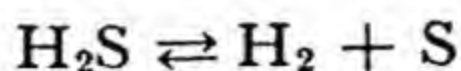
Physical Properties. Hydrogen sulfide is a colorless gas, liquefying at -62° and freezing at -82.9° . Its critical temperature is 100° yet at 10 atmospheres the gas liquefies at 20° . At room temperatures about three volumes dissolve in one volume of water. It readily escapes from water. Its odor is very disagreeable. Air containing 1 part in 1000 is rapidly fatal, thus H_2S is nearly as dangerous as prussic acid but for its warning odor. Since this gas is evolved in some manufacturing processes it is an industrial poison. The gas is about one and one-fifth times as heavy as air, so it can be collected by air displacement. (Why not over water?)

Chemical Properties. A solution of hydrogen sulfide open to the air soon has a film of sulfur on the surface, showing how easily it is oxidized. A rapid oxidation is secured by burning the gas in air:



If a cold dish is held in the middle of the burning jet for a moment, a yellow spot forms. This is sulfur, of course, so it is evident that in the interior of the flame where there is no contact with air the unburned gas has been dissociated by heat because

of the low heat of formation of hydrogen sulfide. The cold surface merely condenses the sulfur vapor before it has opportunity to burn (Fig. 91):



This reaction is reversible, as the two elements are known to unite when heated. The gas cannot be dried by concentrated sulfuric acid because the concentrated acid oxidizes it, but phosphorus pentoxide is a suitable drying agent. Oxidizing agents of all kinds attack hydrogen sulfide.

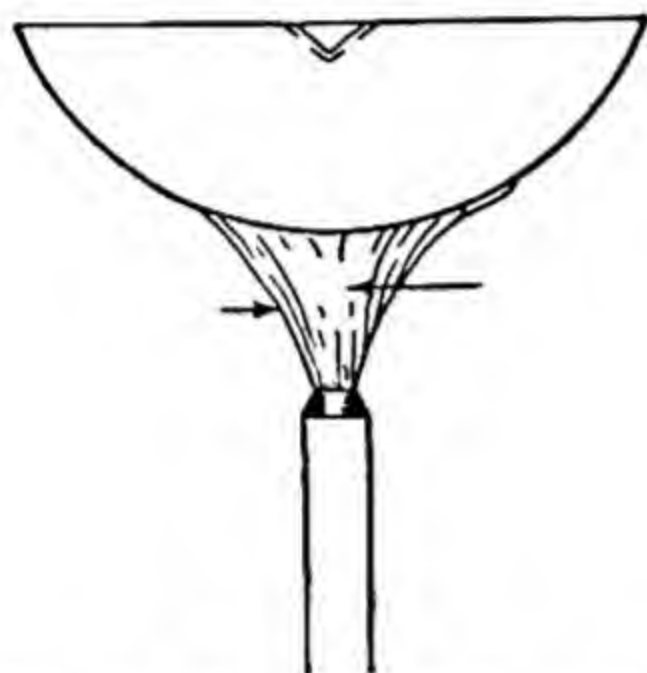
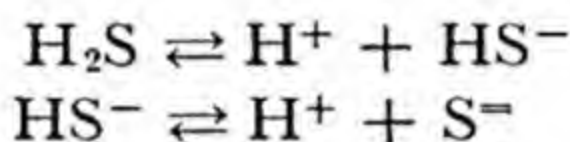


Fig. 91. Cracking H_2S within a hot flame.

3. What are the products when hydrogen sulfide is burned with a large supply of air?

Hydrogen sulfide is an extremely weak acid in water solution. The first hydrogen atom ionizes very little and the second to a minute degree, less than the ionization of water, in fact.

This must indicate a covalent linkage:



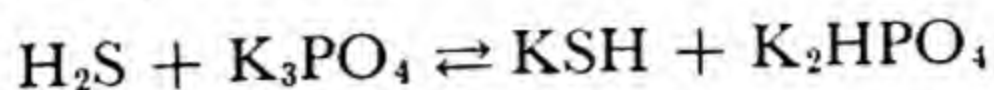
One liter of water saturated with hydrogen sulfide at 25° contains, states Engelder:

0.95×10^{-4}	gram ions of H^+
0.95×10^{-4}	" " " HS^-
1.2×10^{-15}	" " " $\text{S}^=$
0.1 gram mole	" H_2S

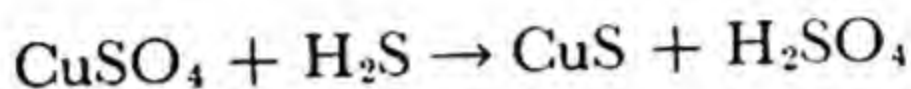
At room temperatures the ionization constants of these two steps are:

$$\begin{aligned}\frac{[\text{H}^+] \times [\text{HS}^-]}{[\text{H}_2\text{S}]} &= K_1 = 10^{-7} \\ \frac{[\text{H}^+] \times [\text{S}^=]}{[\text{HS}^-]} &= K_2 = 10^{-15}\end{aligned}$$

Hydrogen sulfide may be removed from oil refinery gases and liquids by absorption in solutions of K_3PO_4 from which it can later be expelled by heating:



Use in Analysis. Hydrogen sulfide is invaluable in qualitative analysis and useful in quantitative work also. In a solution of copper sulfate, for example, this gas precipitates black cupric sulfide:

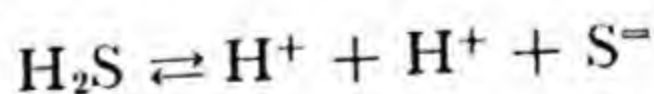


Other sulfides formed in similar ways are black HgS , orange Sb_2S_3 , yellow As_2S_3 and CdS , and white ZnS . In the system of qualitative analysis we divide the sulfides into two great groups:

1. Sulfides insoluble in dilute strong acid (CuS , HgS , As_2S_3 , etc.)
2. Sulfides soluble in dilute strong acid but insoluble in neutral or alkaline solution (NiS , MnS , ZnS , etc.)

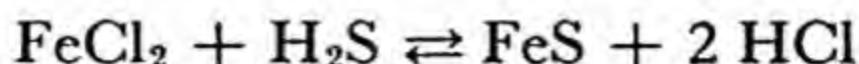
The reason zinc sulfide, for example, is not precipitated in acid solution is that the addition of a strong acid like hydrochloric increases greatly the number of H^+ ions present. This gives infinitely more opportunities for contact between the very few $S^{=}$ ions and H^+ ions, so more $S^{=}$ ions are removed from the field, tied up as HS^- ions or H_2S molecules. This leaves so few $S^{=}$ ions that the Zn^{++} ions do not form enough zinc sulfide molecules to saturate the solution and thus yield a precipitate.

How different if a strong base is added! The great excess of OH^- ions ties up nearly all the H^+ ions and so the equilibrium is displaced to the right, producing an enormous increase in the number of $S^{=}$ ions:



Now there are enough $S^{=}$ ions to react with Zn^{++} ions and form more zinc sulfide than the solution will hold, and precipitation occurs. The sulfides of copper and other metals of its group are so insoluble in water that they can be precipitated in spite of the suppression of ionization of hydrogen sulfide by a strong acid.

On the other hand ferrous sulfide is so susceptible to the action of acid that it cannot be precipitated by passing hydrogen sulfide into a ferrous salt solution:



At equilibrium the reaction to the left is favored strongly. The hydrochloric acid formed may be said to dissolve the sulfide. It really suppresses the ionization of the hydrogen sulfide so that the Fe^{++} ions with the S^- ions (now in very low concentration) fail to form enough FeS to saturate the solution. But if we add a base the acid is neutralized and ferrous sulfide precipitates at once.

The ionization constant of hydrogen sulfide is, of course, very small:

$$\frac{[\text{H}^+]^2 \times [\text{S}^-]}{[\text{H}_2\text{S}]} = K$$

The solubility product of $[\text{Cu}^{++}] \times [\text{S}^-] = K_1$ is extremely small, easily exceeded even in N HCl. The solubility product of $[\text{Zn}^{++}] \times [\text{S}^-] = K_2$ is not quite so small, so precipitation of ZnS by H_2S is never complete. The solubility product of $[\text{Fe}^{++}] \times [\text{S}^-]$ is so much larger that it can never be exceeded by use of H_2S in a solution of a ferrous salt.

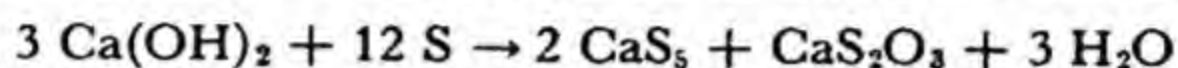
The sulfides of arsenic, antimony, tin, mercuric mercury, copper, cadmium, and bismuth are precipitated by H_2S from a solution 0.3 N in terms of HCl. Yet if ions of cobalt, nickel, manganese, and zinc are present in this solution their sulfides will not precipitate. This means that the sulfide-ion concentration, even when 0.3 N acid represses the weak ionization of H_2S , is sufficient to help exceed the relatively small solubility products of As_2S_3 , Sb_2S_3 , SnS , HgS , CuS , CdS , and Bi_2S_3 , but not sufficient to help exceed the somewhat larger solubility products of CoS , NiS , MnS , and ZnS . The common systems of qualitative analysis use this distinction in group separations.

In certain instances calculation of ionic concentrations would indicate that the solubility products would be exceeded yet no precipitation occurs. Such ions as Zn^{++} , Cd^{++} , and Cu^{++} form complex ions in sufficient amount to reduce the simple ion concentration to values so small that the solubility products are not exceeded.

is a famous one. "Yellow" ammonium sulfide, $(\text{NH}_4)_2\text{S}_x$, is a reagent in qualitative analysis and is more red than yellow to tell the truth.

If acid is poured into a solution of a polysulfide, free sulfur is formed and hydrogen sulfide escapes (write the equation).

It is possible that in lime-sulfur sprays the following reaction takes place:



Sodium polysulfide reacts with ethylene chloride ($\text{C}_2\text{H}_4\text{Cl}_2$) to form thiokol, one of the synthetic rubbers.

Exercises

7. Prove that at least a few S^- ions are found in a water solution of H_2S .
8. What volume of H_2S at 20°C . and 750 mm. may be produced by the action of HCl on 100 g. of FeS ?
9. How many milliliters of H_2S will precipitate the copper in 100 ml. of a $\text{N}/10$ solution of a cupric salt?
10. Explain in terms of solubility products why the hydroxides of Fe^{+++} (but not Fe^{++}), Al , and Cr are precipitated by NH_4OH even if the ionization of that weak base is repressed by NH_4Cl while the same reagents fail to precipitate the hydroxides of divalent Co , Ni , Mn , and Zn .
11. Solutions of Na_2S are powerfully basic, while those of NaHS are much less so. Explain.
12. The sulfur atom forms complexes by a ready sharing of outer electrons $\ddot{\text{S}}:$ in an effort to complete its octet layer. Diagram the molecule S_2 .
13. Diagram the H_2S molecule, using dots to indicate the number of electrons in the outer shell of each atom.
14. Pass H_2S into a bottle half-filled with water. Stopper and shake. Smell. Add bits of red and blue litmus paper to the liquid. Then add plenty of sodium hydroxide solution and shake. Finally smell. Explain.

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Chapter 25 SULFURIC ACID AND THE OXIDES OF SULFUR

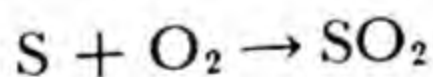
This chapter will deal mainly with sulfur dioxide and trioxide, and with sulfurous, sulfuric, and thiosulfuric acids.

SULFUR DIOXIDE

Sulfur dioxide is not a recently discovered gas. It was mentioned in Homer's time as a disinfectant; and Paracelsus, the alchemist, knew something of its bleaching powers. Priestley first made it in pure form and recognized it as a definite compound (1775). It occurs in volcanic gases and in some spring waters.

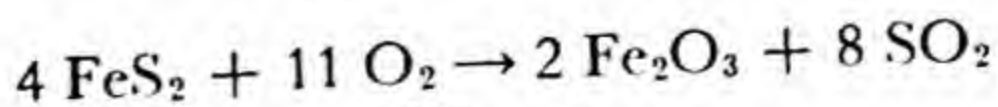
Preparation.

1. Burning Sulfur. Sulfur burns in air with a pale blue flame, forming sulfur dioxide. In the United States this is a great commercial method of preparation:

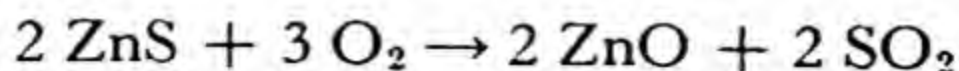


2. Roasting Sulfide Ores. This is one of the common commercial sources of sulfur dioxide. Many metals occur as sulfides which when roasted produce gases dangerous to vegetation and to health. In some states laws forced the smelters to prevent this nuisance. As a result many smelters have constructed sulfuric acid plants to utilize the waste sulfur dioxide, so everyone has profited.

The cheapest sulfide ore is iron pyrites (FeS_2), which burns like coal:



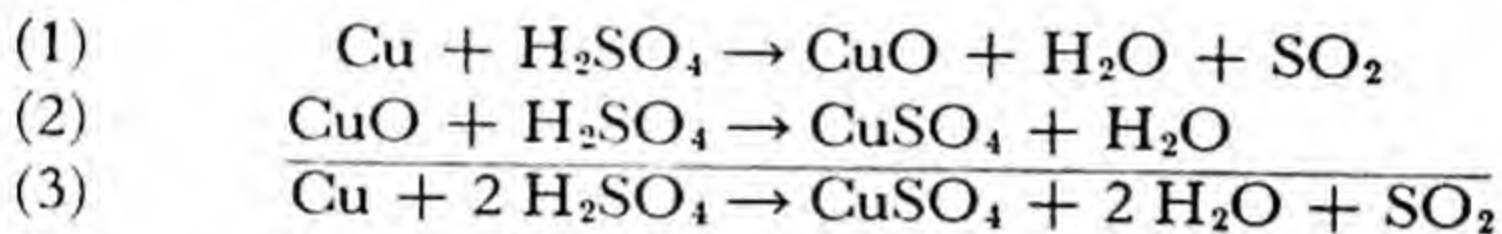
Zinc sulfide (ZnS) must be fed preheated air:



Sulfur dioxide obtained from the roasting of sulfide ores is, of course, diluted with several volumes of nitrogen from the air.

At one time we burned iron pyrites, FeS_2 (largely imported from Spain), to secure sulfur dioxide for oxidation to sulfuric acid. Now, by means of special burners, we make most of the acid from sulfur dioxide prepared by burning sulfur.

3. Reduction of Sulfuric Acid. Hot, concentrated sulfuric acid readily gives one oxygen from each molecule to metals and other reducing agents. In fact under some conditions it has been known to give up all of its oxygen:



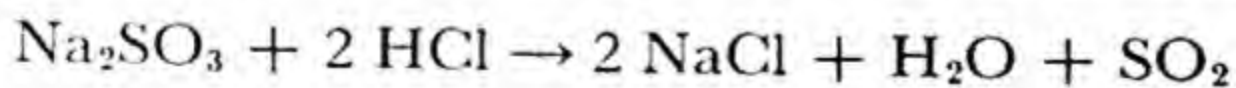
Carbon may be used, or even sulfur, instead of copper:



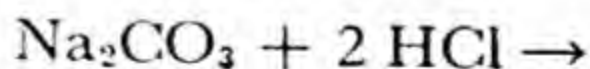
Exercises

1. Write the equation for the oxidation of sulfur by hot concentrated sulfuric acid.
2. In 1775 Priestley broke a thermometer in hot concentrated sulfuric acid — and smelled sulfur dioxide. Explain.

4. Acids on Sulfitcs. A simple laboratory method of preparation is found in the slow dropping of some dilute acid on sulfitcs. The gas may be dried over anhydrous calcium chloride:



Compare:

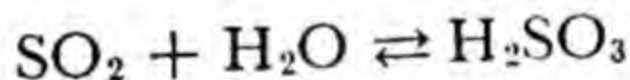


Physical Properties. Sulfur dioxide is a colorless gas with a peculiar choking odor. Eighty volumes dissolve in one volume of

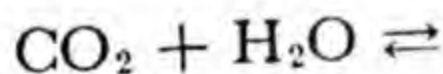
water at 0° and 760 mm. It is 2.2 times as heavy as air and is easily liquefied under three atmospheres' pressure at 20° . In fact an ice-salt mixture will liquefy it at ordinary pressures. The liquid boils at -10° and freezes at -76° into a snowlike solid. It is conveniently kept in steel cylinders for laboratory use. Liquefied sulfur dioxide is, like pure water, a poor conductor of electricity but certain salts and SOCl_2 dissolved in it conduct well. Furthermore reactions between such compounds dissolved in liquid SO_2 occur as in water, convincing us that ionization takes place. (SOCl_2 is thionyl chloride while SO_2Cl_2 is sulfuryl chloride.)

Liquid sulfur dioxide is a good solvent for iodine, sulfur, and phosphorus. Potassium iodide dissolves in liquid sulfur dioxide. On evaporation of the solvent red crystals of $\text{KI} \cdot 4 \text{SO}_2$ are obtained but after standing in the air for some time only white potassium iodide remains.

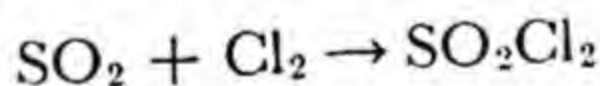
Chemical Properties. Sulfurous acid and sulfur dioxide are both present in equilibrium in a water solution of this gas:



Compare



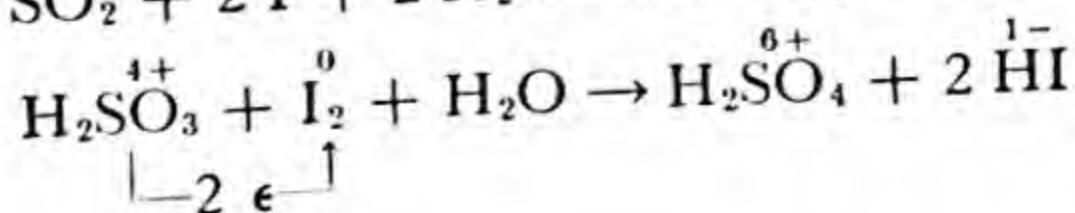
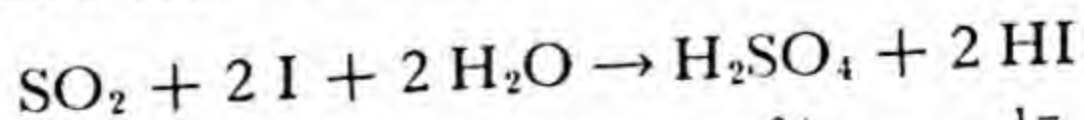
Sulfur dioxide reacts with chlorine to form sulfuryl chloride:



In addition to its reaction with water, with chlorine, and with hydrogen sulfide, sulfur dioxide unites with oxygen to form sulfur trioxide, a reaction aided greatly by suitable catalysts.

3. What is the reaction with hydrogen sulfide?

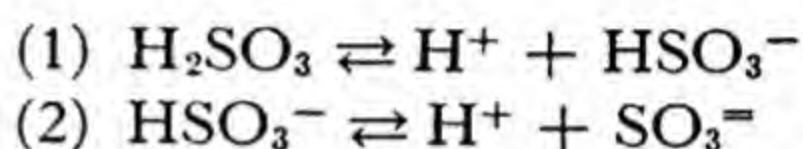
Sulfur dioxide may be determined quantitatively by reaction with a standard iodine solution using starch paste as indicator:



Uses. Sulfur dioxide is used to some extent as a refrigerant (because it is volatilized and liquefied at convenient temperatures). Huge quantities are necessary to the manufacture of sulfuric acid and of calcium sulfite for paper making. A great deal is used in bleaching and some in fumigation, although formaldehyde has almost displaced it from that field. Sulfur dioxide has come into recent use (in low concentration) to prevent ignition

of magnesium and its alloys during casting and heat treatment.

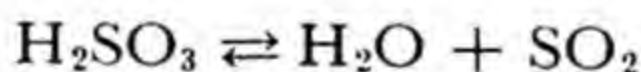
Sulfurous Acid. Sulfurous acid is a weak acid ionizing in two stages:



Reaction (1) proceeds to the right to a slight extent and reaction (2) to a minute extent.

Addition of OH^- ions from a

strong base disturbs both these equilibria to the right. Sulfurous acid is also very unstable, like H_2CO_3 :



4. To remove excess chlorine after a fabric has been bleached with that substance an "antichlor" is added. "Hypo" and sulfurous acid or sulfites are used. Write the equations showing how sulfurous acid in water uses up the free chlorine.

The reaction of SO_2 with water is much more rapid than for CO_2 .

The shape of the SO_2 molecule is angular while CO_2 is linear and the products of both reactions are triangular. Test with phenolphthalein solutions for time of color change.

Sulfites and Bisulfites. If an excess of sulfur dioxide is bubbled through a solution of a base such as sodium hydroxide, an acid salt called sodium bisulfite is formed:

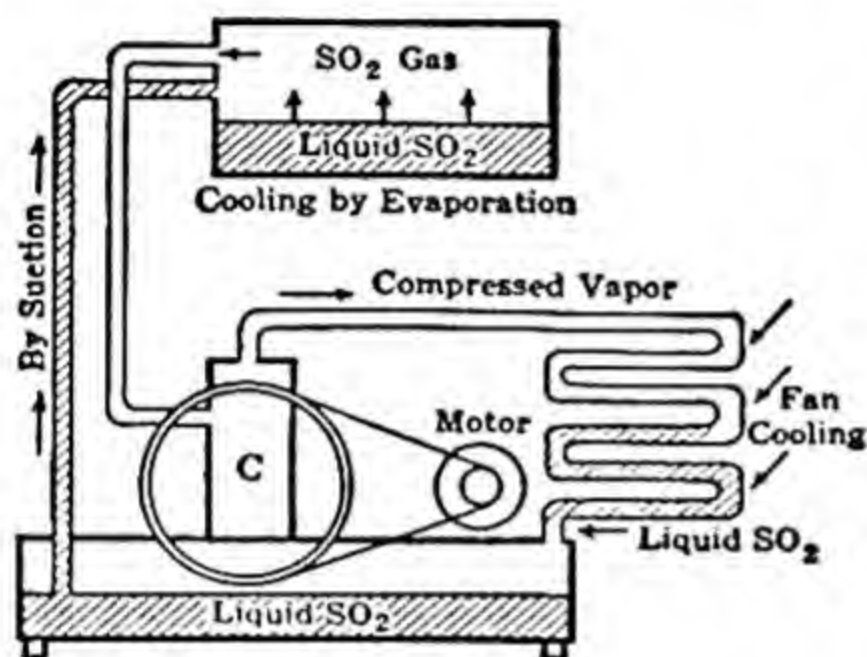
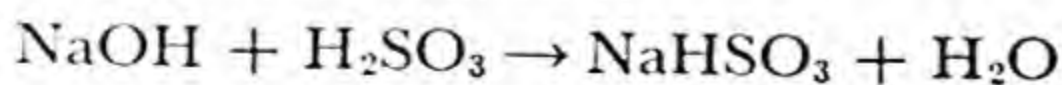
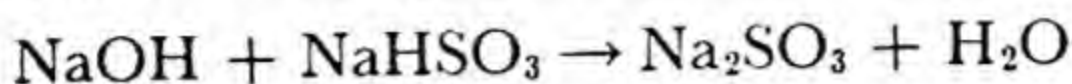


Fig. 92. Refrigeration with SO_2 .
(After Deming.)

This reminds us of the similar reaction of hydrogen sulfide. And just as with that reaction, addition of an equivalent amount of the base to the solution of bisulfite forms the normal sulfite:

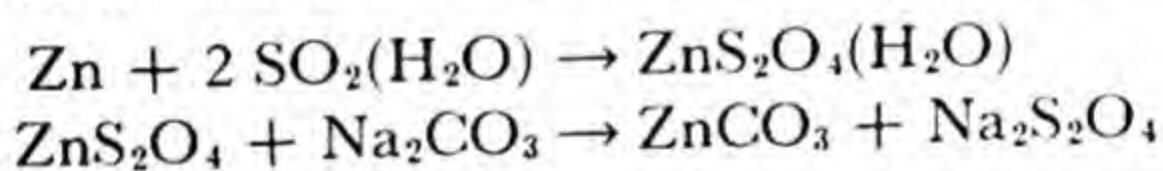


Calcium bisulfite, $\text{Ca}(\text{HSO}_3)_2$, is one of the most important of these salts because of its ability to dissolve the lignin which cements the fibers of cellulose in wood. Chips of soft woods are heated in bisulfite solutions and the cellulose fibers are separated to be used as paper pulp.

5. How is calcium bisulfite made?

Sodium thiosulfate ("hypo"), $\text{Na}_2\text{S}_2\text{O}_3$ is discussed with Sodium Salts.

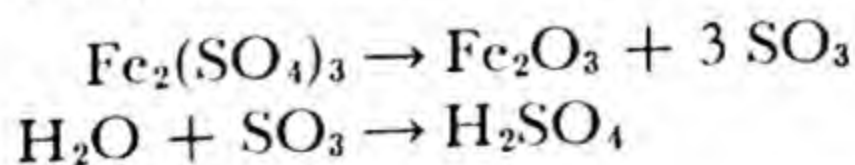
Sodium Dithionite (Hydrosulfite). Sulfurous acid is reduced by zinc to yield zinc dithionite, ZnS_2O_4 . The similar sodium salt is used to the extent of millions of pounds yearly to change insoluble indigo blue to soluble indigo white. This penetrates fabrics to be dyed and by later oxidation becomes fixed as the insoluble blue. The dithionites are very powerful reducing agents:



Sulfur Trioxide. Sulfur trioxide is a colorless liquid boiling at 46° and freezing at 15° . It reacts with water to form sulfuric acid. Under sulfuric acid we discuss its formation by the catalytic oxidation of sulfur dioxide.

SULFURIC ACID

Sulfuric acid was much used by the alchemists. Basil Valentine, in the fifteenth century, secured sulfur trioxide and the acid by distilling ferric sulfate, and Geber writes of making it from other sulfates in the thirteenth century:



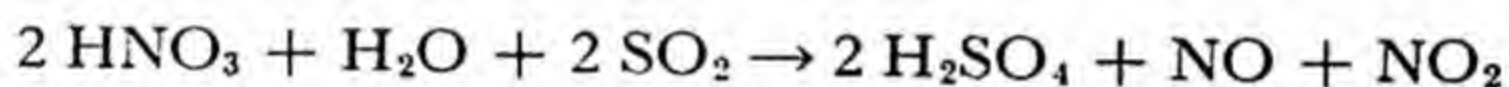
Yet the manufacture of this great acid, the most important compound made by man, was not put on a commercial basis before

1740. Then sulfur and "niter" (KNO_3) were burned together in the presence of air in glass globes. In 1793 the oxidation process was made continuous by the employment of oxides of nitrogen as a catalyst.

Gay-Lussac towers were first used in 1827 to recover the catalytic oxides of nitrogen, while the Glover tower was developed in 1859.

The industry is now so enormous that the United States usually makes 10,000,000 tons, estimated as 100 per cent acid, in a normal year. There are two rival processes of manufacture, each especially adapted to certain kinds of raw material and each suited to certain concentrations of product.

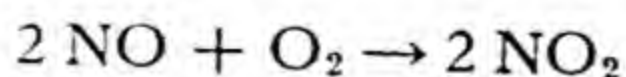
Lead-Chamber Process. The essential reactions in huge towers and lead-walled chambers involve the oxidation of sulfur dioxide to the trioxide in the presence of enough water to form sulfuric acid. A mixture of air and the dioxide reacts very slowly, so nitric acid vapors are introduced to increase the speed of reaction:



The cost of nitric acid would make this process economically impossible were it not for the fortunate fact that the nitrogen dioxide (NO_2) released as a by-product is itself capable of oxidizing sulfur dioxide:

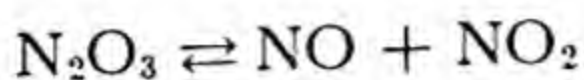


Now another fortunate fact saves the day — and much money. If this nitric oxide (NO), the by-product here, were wasted, the lead-chamber process would soon become historical only. But luckily this nitric oxide has a property — possibly somewhat dry for the student but of thrilling interest to the men owning lead-chamber plants — of rapidly uniting with the oxygen of air to form the useful nitrogen dioxide:



In fact nitric oxide is a catalyst, making the oxygen of air unite with sulfur dioxide in a roundabout way and itself being regener-

ated time after time. The nitric acid, then, is merely a starter — a source of the oxides of nitrogen. Most authorities refer to nitrogen trioxide as the catalyst. However at the temperature of the lead chambers this gas dissociates to a very great extent as follows:



The explanation is quite logical for either gas as catalyst, but it is simpler as given above. There is yet much dispute about these reactions.

As shown in the diagram, Fig. 93, the sulfur dioxide is produced in the burners by roasting some sulfide, usually iron

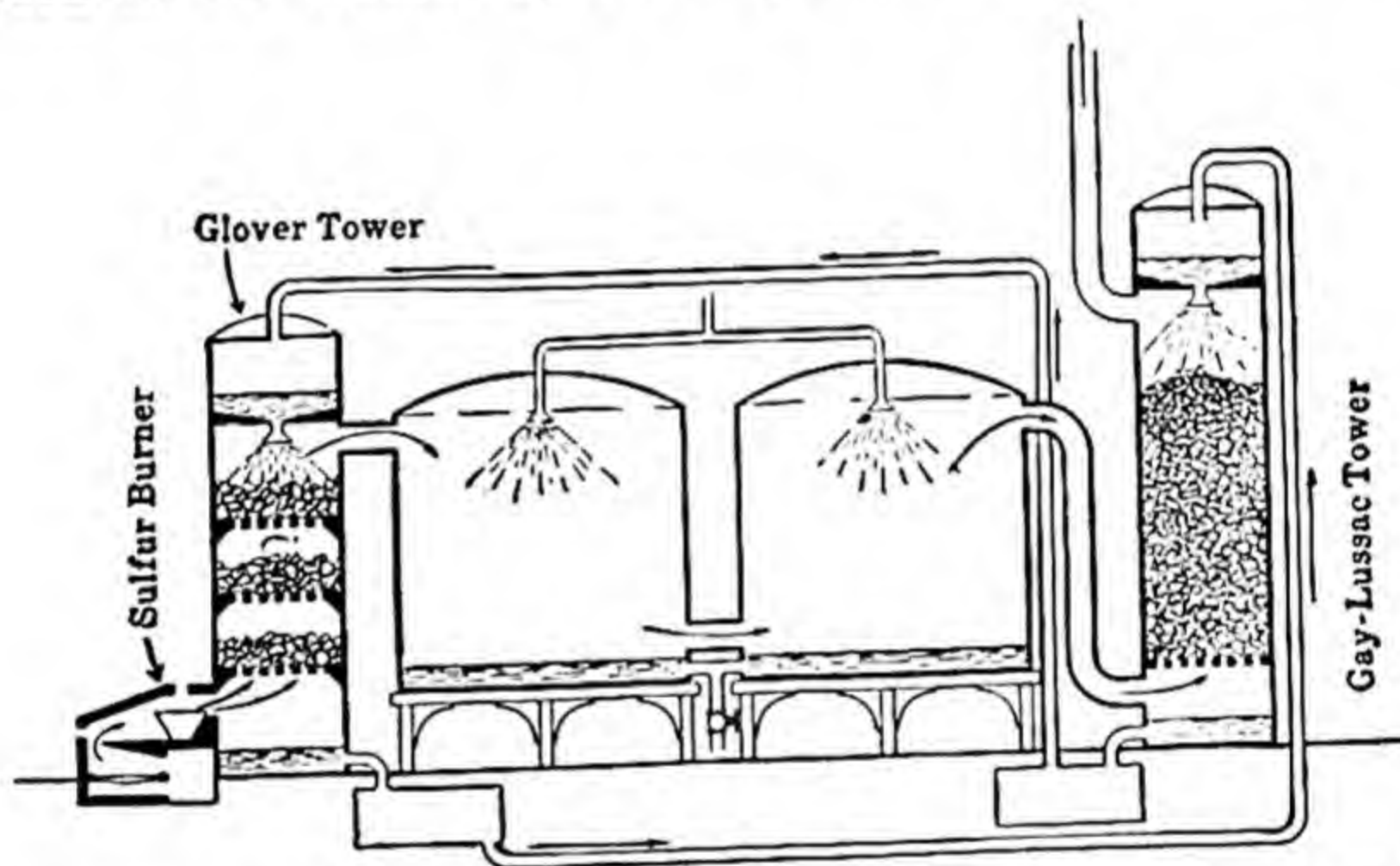


Fig. 93. A lead-chamber plant. Some of the concentrated acid collecting at the bottom of the Glover tower is piped off through a separate opening and sold. Water in the form of dilute acid is led into the top of the Glover tower through an opening not shown in the diagram.

pyrites, in a strong draft of air. However, the modern practice in the United States is to burn sulfur itself in specially designed roasters. Only 20 per cent of our sulfuric acid is now made from pyrites.

The oxides of nitrogen introduced into the Glover tower are prepared by a catalytic oxidation of ammonia.

This mixture — flue gases, nitrogen of air, excess oxygen, sulfur dioxide, and the nitric acid vapors — enters the Glover tower.

This is a tall tower loosely filled with broken tile, coke, or brick which forces good mixing of the gases with the liquid splashing down from the top of the tower.

Possibly about 16 per cent of the total acid of the plant is formed right in this tower and most of it is drawn off for sale.

The liquid introduced at the top is a compound of oxides of nitrogen with concentrated sulfuric acid. Luckily this compound is decomposed by water with instant release of the oxides of nitrogen, ready for work as catalyst. So a stream of concentrated "nitrosyl" sulfuric acid meets a stream of water (really dilute acid) *inside* the tower. Here a nice economy operates. The released oxides of nitrogen (with those from the action of nitric acid) are swept on by the great stream of other gases into the first chamber. But the diluted acid splashing down the tower meets hot gases fresh from the burners, water is evaporated and passes on as steam into the chambers (where it is needed), and the acid, now cheaply concentrated to 62–70 per cent, is tapped off at the base of the tower. Everything goes just where it is needed; apparently nothing is wasted.

The lead chambers, from three to five in number, are huge affairs, the first $75 \times 26 \times 14$ feet, the others smaller. They are really inverted boxes suspended so that their lower edges allow the constant overflow of acid collecting on the floor but do not allow escape of gases except by the stack or Gay-Lussac tower. These chambers are lined with sheets of lead melted together at the edges by oxyhydrogen flames. Lead is used because it is not attacked by acid of the concentration produced in the chambers.

An excess of steam is used in the chambers for two reasons. First, if the sulfuric acid forming and collecting on the floor were concentrated, it would take up the catalyst, thus stopping the whole process. Second, the lead walls would be attacked by acid of high concentration. So the "chamber acid" is of only 62–70 per cent concentration. This corresponds to a specific gravity of 1.5–1.62. A commercial measure of sp. gr. is "degrees Bé.," and 60° Bé. is 77.67 per cent acid.

To give the gases full opportunity to react a series of three to

five chambers is provided and even then some sulfur dioxide is lost. The great volume of atmospheric nitrogen present forces the use of a chimney or stack, and this is made in the form of the Gay-Lussac tower, resembling the Glover tower. Oxides of nitrogen released at the end of the last chamber would be lost to the air, ruining the process, but for the clever use of the fact that concentrated acid reacts with these oxides, forming a solution of nitrosyl sulfuric acid. The concentrated acid splashes down over the broken tile and is forced from the bottom of the Gay-Lussac to the top of the Glover tower (by compressed air), where it releases its oxides of nitrogen as previously described. Unfortunately not all the catalyst is recovered and continuous replacement from nitric acid is necessary.

Some of the concentrated acid collecting at the bottom of the Glover tower is piped off through a separate opening and sold. Water in the form of dilute acid is led into the top of this tower through an opening not shown in the diagram.

The chamber acid is suitable for use in the manufacture of soluble phosphate fertilizer from phosphate rock, but for most other purposes it must be concentrated. Eventually the rival contact process will make all the concentrated acid, leaving the demand for 62–70 per cent acid to the chamber process. The acid may be boiled down in lead pans or sprayed down a tower against a rising current of hot flue gases to reach a concentration of about 77 per cent. A compact layer of lead sulfate forms in the pans but protects the lead beneath. Acid much above 77 per cent, however, dissolves lead sulfate (hence the presence of a little lead as impurity in commercial acid) and the work must be finished in glass, platinum, or cast iron vessels to give a concentration of about 94 per cent and a specific gravity of 1.84. Although iron is readily attacked by dilute acid, it is not affected by the acid of high concentration — just the reverse of the effect on lead. The expense of concentrating the chamber acid to 95 per cent gives the contact process a great advantage.

6. Without help make a detailed drawing of the lead-chamber plant, using arrows to show the flow of gases and liquids.
7. Why not use six chambers to save loss of oxides of nitrogen?

The Contact Process. A mixture of sulfur dioxide and air is led through a series of iron tubes containing a porous supporting material such as asbestos or magnesium sulfate which holds the catalyst, finely divided platinum. The most favorable tempera-

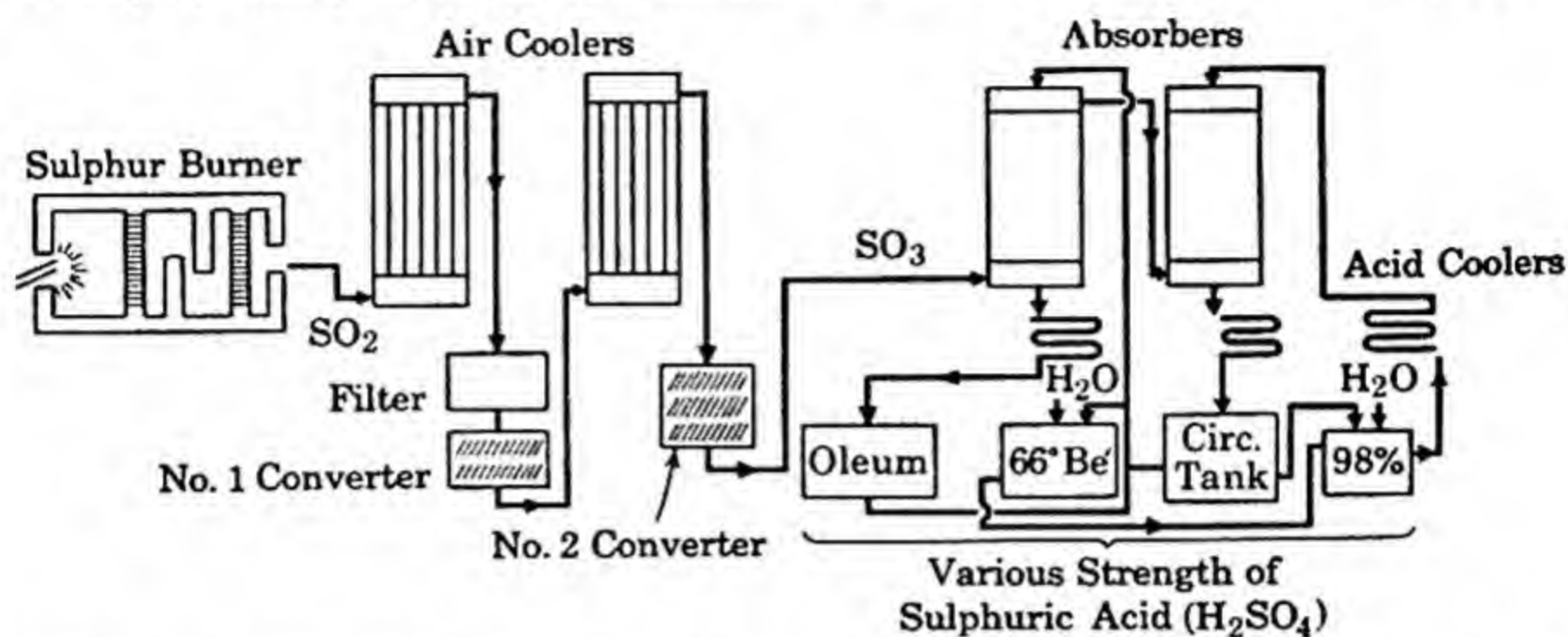


Fig. 94. The contact process. The 66° Be. acid (93.2 per cent) from a lead-chamber plant, by absorption of SO_3 , can be raised to 98 per cent or greater concentration. "Oleum" is a solution of SO_3 in H_2SO_4 . Texas Gulf Sulfur Co.

ture for the platinum catalyst is about 400° . Below this temperature the action is too slow, and above this temperature the equilibrium is displaced in the wrong and costly direction:



Since the reaction desired is exothermic, the catalyst must be cooled somewhat by passing the incoming cold gases around the tubes to hold the temperature below 500° . Sulfur trioxide is decomposed to some extent at 500° , completely at 1000° . It is the universal practice to pass the sulfur trioxide into 98 per cent acid, maintaining that concentration by a sufficient stream of water. This seems absurd until we learn that the gas is not readily absorbed by water. It is profitable to add chamber acid instead of water to maintain the concentration at 98 per cent for this is a cheap way of removing water from the chamber acid. Therefore the two types of plants often work together.

During 1929 compounds or mixtures containing vanadium pentoxide promoted by iron, potassium, etc., came into commercial use as catalysts in contact sulfuric acid plants. The advantages are low cost of the catalyst and freedom from poisoning. The conversion efficiency is higher than with platinum when the catalyst functions at about 500° .

The contact and lead-chamber processes supplement each other. For production of acid of very high concentration and purity the contact process will always be cheaper. In fact, oleum, or "fuming" sulfuric acid (100 per cent acid in which much SO_3

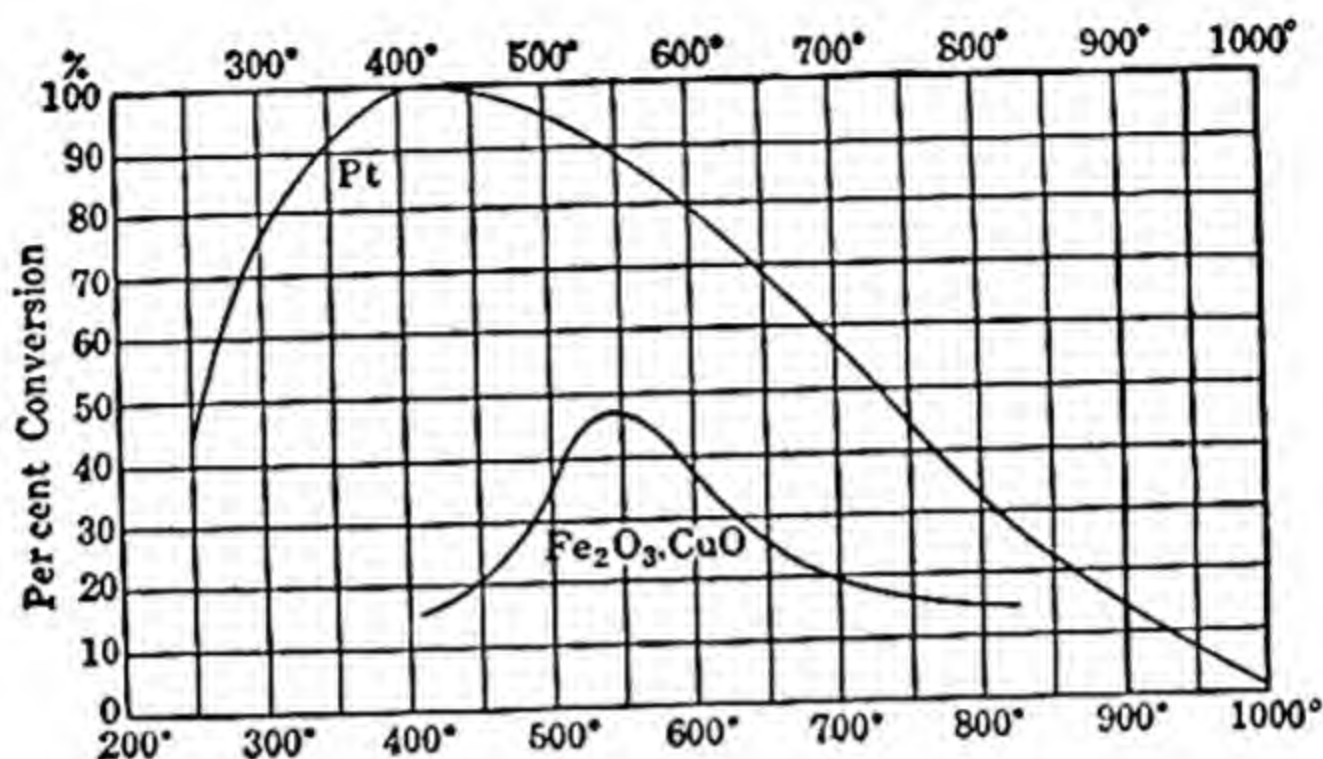


Fig. 95. Per cent conversion of SO_2 into H_2SO_4 at different temperatures.

is dissolved), can be made only by the contact process. For vigorous action in some industries (notably, the manufacture of explosives), no other acid strength will serve. But for production of the crude acid of moderate concentration suitable for acid treatment of phosphate rock in the fertilizer industry, the lead-chamber plant is well adapted. In the United States about 60 per cent of our sulfuric acid is made by the contact process.

Properties of Sulfuric Acid. Pure anhydrous sulfuric acid is an oily colorless liquid ("oil of vitriol") with a density of 1.838 at 15°. It boils at 338° with some decomposition ($\text{H}_2\text{SO}_4 \rightleftharpoons \text{SO}_3 + \text{H}_2\text{O}$). As the gases cool they combine again, forming droplets of sulfuric acid with the appearance of dense, white fumes. The constant-boiling acid is 98.33 per cent. Decomposition is marked at 100° and complete at 450°.

Sulfuric acid mixes in all proportions with water with the evolution of much heat. To avoid sudden generation of steam and consequent spattering the concentrated acid is always slowly poured into the water (which quietly absorbs the heat, especially if stirred). The *oxidizing power* of hot, concentrated acid has already been discussed; also its *dehydrating power*.

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The large amount of heat evolved on mixing sulfuric acid and water is due mainly to the formation of a hydrate, $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$. There are two other hydrates, $\text{H}_2\text{SO}_4 \cdot 2 \text{H}_2\text{O}$ and $\text{H}_2\text{SO}_4 \cdot 4 \text{H}_2\text{O}$.

NORMAL ANNUAL USE OF SULFURIC ACID IN U. S. BY INDUSTRIES (100 PER CENT)

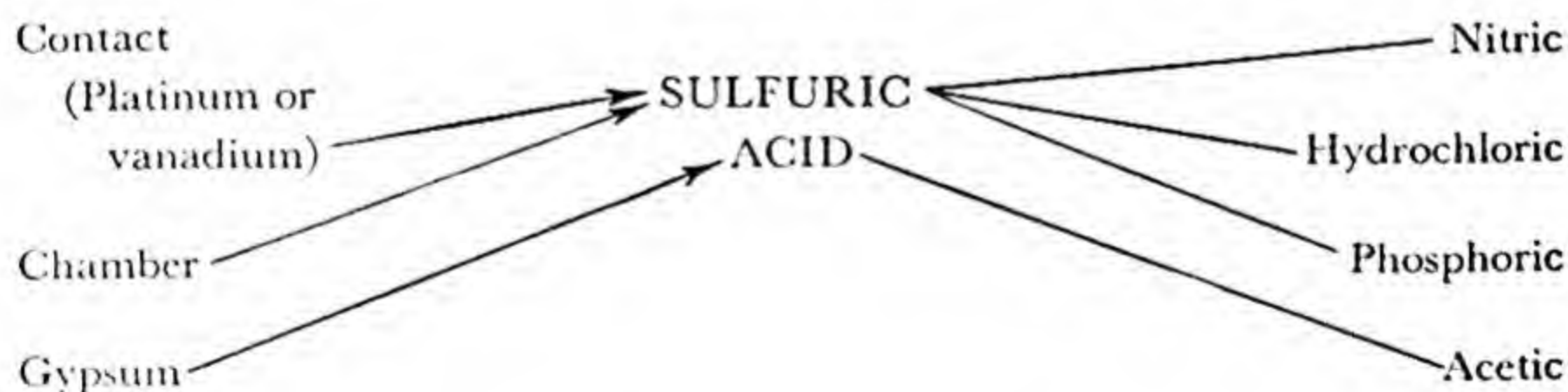
Fertilizers	3,510,000 tons
Petroleum Refining	1,065,000
Chemicals	1,970,000
Dyes and Coal Products	630,000
Steel Pickling	550,000
Metallurgical Uses	315,000
Paints, Pigments	665,000
Explosives (industrial)	115,000
Rayon and Cellulose Film	610,000
Textiles	73,000
Miscellaneous	400,000
Total	9,903,000

During war years the total was probably 50 per cent greater due largely to the enormous demand for explosives.

Competition

Processes to make:

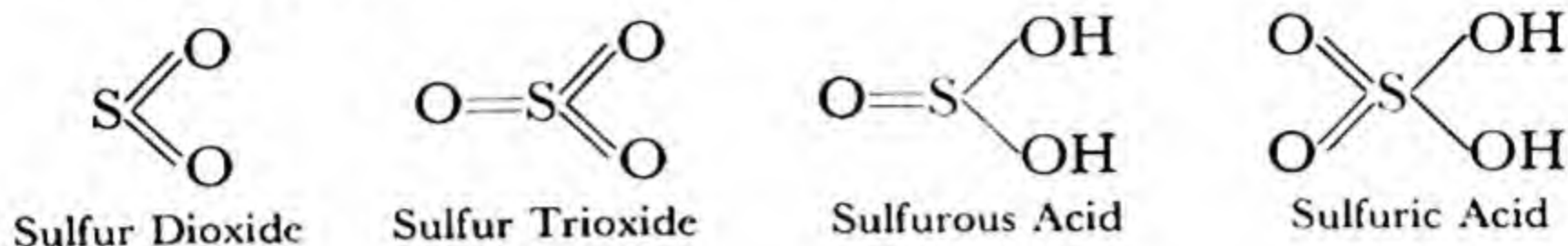
In competition with:



Uses. The petroleum industry was the first to demand huge quantities of sulfuric acid for the removal of unsaturated compounds that darken by oxidation in air. Much chamber acid is used by fertilizer factories as a means of converting calcium phosphate rock into soluble acid phosphate. The manufacture of nitroglycerin and smokeless powder calls for a large tonnage, so it is evident that this great acid is indispensable in war, as it is

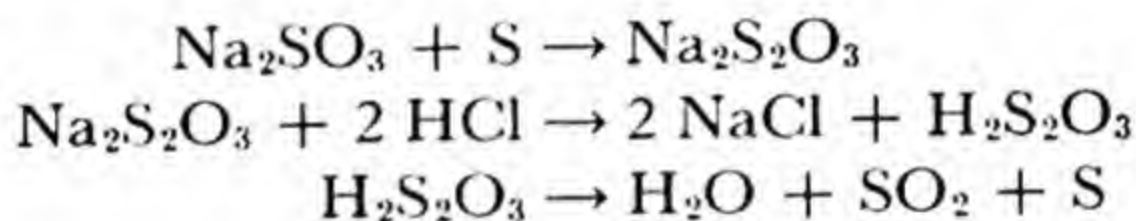
at any time to make possible mining and excavations for railways. The acid is also used to remove oxide scale from steel wire and sheet.

Structure of the Oxides and Acids of Sulfur.



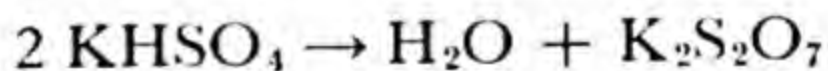
The electron valence shell formulation represents SO_2 as $:\ddot{\text{O}}:\ddot{\text{S}}::\ddot{\text{O}}:$. Here the sulfur atom with six valence electrons $:\ddot{\text{S}}:$ donates a pair to one oxygen atom (coordinate bond), and shares two electrons with the other oxygen atom (double covalent bond). The apparent valence, or valence number, of sulfur in SO_2 is four.

Other Acids of Sulfur. When sulfur is boiled with a solution of a sulfite it adds on directly, forming a salt of *thiosulfuric acid*. The free acid is unstable:

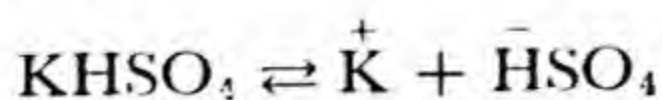


The name indicates that the acid differs from sulfuric acid in containing one sulfur atom in place of the fourth oxygen. The sodium salt is the photographer's "**hypo**." "Hypo" reacts with free chlorine, and so is a good "antichlor" after bleaching.

Pyrosulfuric Acid, a good oxidizing agent, is formed when sulfuric acid and sulfur trioxide are brought together in molecular proportions. Its salts are easily prepared by heating acid sulfates:

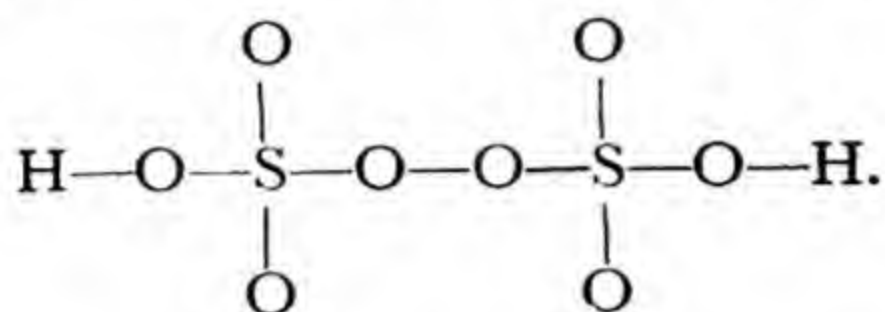


Persulfuric Acid ($\text{H}_2\text{S}_2\text{O}_8$) is a rather modern oxidizing agent of great power. Electrolysis of a cold concentrated solution of an acid sulfate with a platinum wire as anode produces the salts of persulfuric acid. The acid sulfate ionizes as follows:

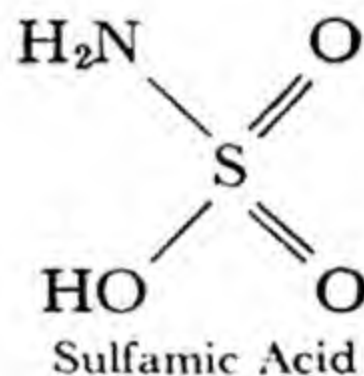
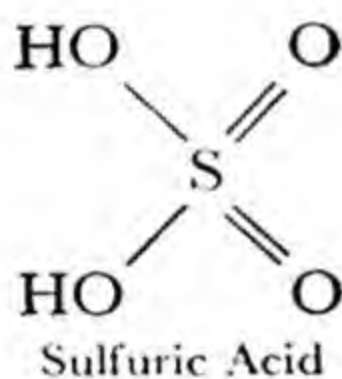


The HSO_4^- ions, on discharge at the small anode (high current density), unite with each other to form $\text{H}_2\text{S}_2\text{O}_8$. The acid potassium sulfate present promptly reacts with this unstable acid to form the sparingly soluble potassium persulfate, $\text{K}_2\text{S}_2\text{O}_8$. Ammonium persulfate is finding some use in photography and as a general oxidizing agent.

A formula suggested for persulfuric acid, $\text{H}_2(\text{SO}_4)_2$, is



Sulfamic Acid, $\text{HSO}_3\cdot\text{NH}_2$. This moderately strong acid is made by the action of fuming sulfuric acid on urea, $\text{CO}(\text{NH}_2)_2$, and hydrolysis of the product.



Its ammonium salt has recently come into extensive use as a fireproofing agent and weed killer. The calcium and barium salts are very soluble, unlike the sulfates.

Fluosulfonic Acid, HSO_3F , has some use in preparing organic compounds. It is a colorless liquid, fuming in moist air and boiling at 165.5° . Most of its salts are soluble in water.

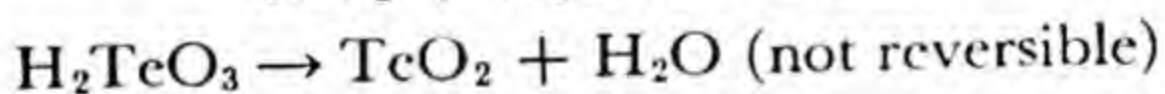
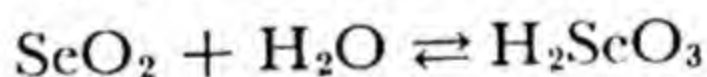
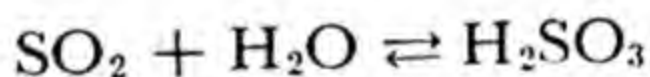
SELENIUM AND TELLURIUM

Similarity of Sulfur, Selenium, and Tellurium. These three elements resemble each other in many respects, and between sulfur and selenium the likeness is remarkable. In fact, selenium usually occurs associated with sulfur in metallic sulfides. All three elements form similar compounds with hydrogen and oxygen, and their acids and salts are much alike. Valences are the same for the three elements.

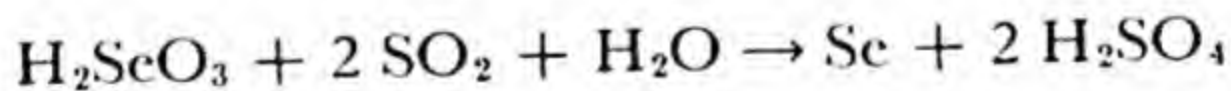
COMPOUNDS OF SULFUR, SELENIUM, AND TELLURIUM

H ₂ S	Hydrogen sulfide	H ₂ Se	Hydrogen selenide	H ₂ Te	Hydrogen telluride
SO ₂	Sulfur dioxide	SeO ₂	Selenium dioxide	TeO ₂	Tellurium dioxide
H ₂ SO ₃	Sulfurous acid	H ₂ SeO ₃	Selenious acid	H ₂ TeO ₃	Tellurous acid
Na ₂ SO ₃	Sodium sulfite	Na ₂ SeO ₃	Sodium selenite	Na ₂ TeO ₃	Sodium tellurite
H ₂ SO ₄	Sulfuric acid	H ₂ SeO ₄	Selenic acid	H ₂ TeO ₄	Telluric acid
Na ₂ SO ₄	Sodium sulfate	Na ₂ SeO ₄	Sodium selenate	Na ₂ TeO ₄	Sodium tellurate

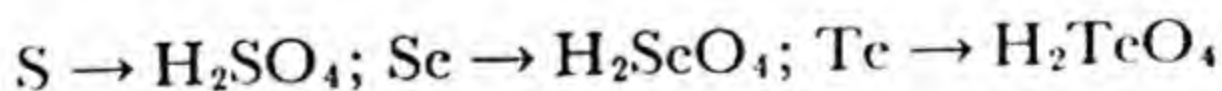
The comparison in the above table is worth noting. All three elements burn with pale blue flames to form the dioxides. Although sulfur dioxide is a gas, the other two are white solids, observed as a smoke when the elements burn. The oxides of sulfur and selenium react with water, but so far it has not been possible to hydrate the oxide of tellurium directly:



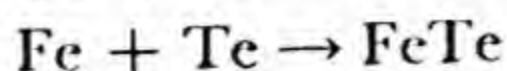
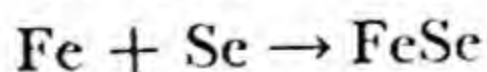
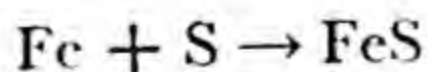
Both selenous and tellurous acids are easily reduced to the element:



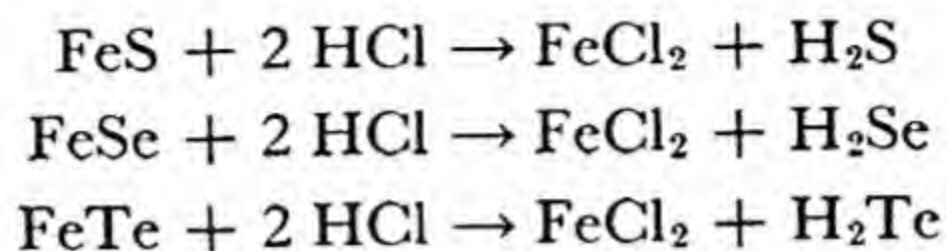
Strong aqueous oxidizing agents convert the elements into sulfuric, selenic, and telluric acids:



Each of the three elements reacts directly with metals when heated:



When these compounds are acidified poisonous gases of offensive odor are released:



Although hydrogen sulfide has an offensive odor, hydrogen selenide is worse; it smells like rotten horseradish.

Selenium. Selenium is non-metallic and exists in allotropic forms. The red form is obtained by the reduction of selenous acid solutions and the black form by melting the red.

Berzelius discovered this element (1817) in the flue dust of pyrite burners. Selenium colors glass a rose-red and so can neutralize the green tint of ferrous iron impurities. During World War I the importation of Brazilian manganese ores into the United States was cut off through lack of ships. Selenium replaced manganese dioxide as a glass decolorizer, and has now been adopted as the standard by the glass industry of the world. Manganese dioxide is cheaper but not so reliable in use. The annual yield of selenium from the copper slimes (from electrolytic refining) is large. Red signal glass is made with selenium.

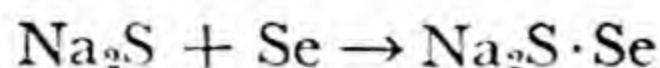
In counteracting the green due to iron impurities in common glass selenium is helped by the presence of a trace of cobalt oxide. A colorless glass results. Since elemental selenium volatilizes at the melting point of glass the non-volatile sodium selenite is used. If as much as 0.25 of one per cent of selenium is present in glass under oxidizing conditions a beautiful ruby glass results.

Selenium insecticides are toxic to some plants, and foods grown on soils containing selenium have toxic effects on animals.

Selenium compounds in lubricating oils will reduce the formation of gums and sludge.

Some magnesium alloys are protected from corrosion in sea water by their selenium content.

Sulfoselenides resemble polysulfides:



This compound reminds us of Na_2S_2 .

One million pounds of cadmium sulfoselenides, $\text{CdS} \cdot \text{Se}$, were used last year as brilliant pigments (for paint) ranging from orange to yellow.

Tellurium. Tellurium is rather plentiful as gold telluride in Colorado and other mining districts, but the small quantities made, 200,000 lbs. yearly, have been extracted from the anode mud of electrolytic copper refining.

At least one use for tellurium has recently been discovered. Only 0.1 per cent tellurium alloyed with lead makes the lead harder and gives it greater resistance to strain and to chemical corrosion. As little as four grams of tellurium in one ton of iron gives greater wear resistance to iron car wheels.

The tellurium vapor lamp may become important. Its high operating temperature, requiring a quartz tube, is a serious disadvantage, yet its light is very nearly like sunlight. The color may be varied with the temperature and pressure. Other uses will be discovered.

Tellurium dioxide is only slightly acidic; consequently salts formed by the union of TeO_2 with acids, even strong acids, are hydrolyzed on dilution, all the more because of the insolubility of tellurous acid, and its weak ionization.

THE SULFUR TRIAD

	ATOMIC WEIGHT	MELTING POINT	BOILING POINT	DENSITY G. ML.
S (rhombic)	32.066	112.8°	444.6°	2.07
Se	79.96	217°	688°	4.8
Te	127.61	452°	1390°	6.0

Exercises

- What volumes of H_2S and SO_2 (standard conditions) will react to give 340 g. of sulfur?
- What weight of sulfur dioxide can be prepared from 150 g. of sodium sulfite (95 per cent pure) and sulfuric acid?
- What weight of pure sulfuric acid can be made from 1000 tons of pure sulfur?
- How could you distinguish between a sulfide, a sulfite, a thiosulfate and a sulfate (if all were soluble)?

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12. Start with hydrogen, oxygen, sodium, calcium, carbon, chlorine, sulfur, platinum and feel free to use heat or light. What compounds can you make, using these elements? How would you do it? Omit platinum compounds.
13. At one time in England starch was treated with very dilute sulfuric acid (instead of pure hydrochloric acid) in order to convert the starch into glucose for the brewer. Many cases of lead poisoning developed among beer drinkers. What was the source of the lead?
14. By injecting less water into the lead chambers and towers the acid settling to the bottom of the chambers would be more concentrated than the product now made (60–70 per cent). Why not do this and get more money per ton?
15. When solid KHSO_4 is heated strongly in a crucible SO_3 is evolved and fumes strongly in moist air. What is left in the crucible?
16. What weight of sulfur dioxide will convert 21 kg. of calcium hydroxide into calcium bisulfite, $\text{Ca}(\text{HSO}_3)_2$?
17. What is the outstanding use of ammonium sulfamate?
18. Why does the lead chamber process of making sulfuric acid continue to compete with the more modern contact process?

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Chapter 26 THE PERIODIC SYSTEM. ATOMIC NUMBERS

Ever since the establishment of the atomic theory by Dalton and Berzelius, chemists have looked for some relation between the atomic weights of the elements and their properties. The development of this relation was delayed a half century because the conception of the atom became increasingly vague in spite of the brilliant work of Dalton, Berzelius, and Avogadro.

After Cannizzaro showed the necessity of reasoning from Avogadro's hypothesis in the development of any system of atomic weights the epochal work of Mendeleeff and Meyer in 1869 became possible. As Wadmore says, "prior to this epoch, errors and inconsistencies must necessarily have masked any general relation between the properties and atomic weights of the elements, though vestiges of such a regularity had been observed."

The first ray of light on this subject appeared in 1829, when Döbereiner observed that several groups of three elements each could be so arranged that the atomic weight of one was the average of the other two, and in all such cases the three elements strikingly resembled each other in properties. Chlorine (35.5), bromine (79.9), and iodine (126.9) show these relations, as the student well knows by this time. The relations are just as convincing for sulfur (32), selenium (79.9), and tellurium (127.6). Calcium (40.1), strontium (87.6), and barium (137.4) resemble each other very closely indeed.

The acceptance of Cannizzaro's ideas on atomic weights put new life into *Döbereiner's triads* of 1829. Then in 1863 Newlands, an English chemist, announced a further-reaching relation. He

arranged the elements, beginning with lithium (not hydrogen), in order of increasing atomic weight and found that "the eighth element, starting from a given one, is a kind of repetition of the first, like the eighth note of an octave in music":

Li	Be	B	C	N	O	F
6.94	9.02	10.82	12.01	14.01	16	19
Na						
23, etc.						

Newlands read his paper before the Chemical Society of London and it was ridiculed by many chemists. Twenty-one years later he was honored with the Davy medal for his vision.

Although apparently unaware of Newlands' ideas, it was only a few years later (1869) that the great Russian, Mendeleeff, out-

lined the periodic relations much as we know them today. Quite independently the German, Lothar Meyer, made a similar discovery, and the credit should be divided. Mendeleeff developed the "periodic law" more fully and brilliantly than Meyer. His short table, modified and brought up to date, is opposite p. 292. As he stated the law, "The whole of the properties of the elements, both chemical and physical, vary in a periodic fashion with their atomic weights."

The column headed "Group O" was unknown to the authors of the system. Proceeding from lithium to the right, the chemi-

cal and physical properties steadily change. If we went no further than fluorine, we might insist that any property of the elements changes steadily with increase in atomic weights. But such a



Fig. 96. Russian stamp honoring Mendeleeff.

theory would be rejected upon proceeding to the heavier element, sodium. The base-forming property steadily decreases from lithium to fluorine, but with sodium it returns in full strength. Beginning a new period of eight with sodium, the base-forming property, for example, again decreases until potassium is reached. But potassium hydroxide is a still stronger base than sodium hydroxide. In other words *the properties of the elements are periodic functions of their atomic weights*.

The table is so arranged that the ninth, seventeenth, etc., elements begin new horizontal rows or periods. It is seen at once that elements in the same vertical column resemble each other in valence number, base-forming properties, etc. Lithium, sodium, potassium, rubidium, and cesium are all monovalent, their hydroxides are strong, and nearly all their compounds are soluble. Moreover the free metals all react violently with water, displacing hydrogen. It can be no accident that an arrangement in periods of eight brings these elements in the same vertical column or "Group," as we call it. Nor is it an accident that sulfur, selenium, and tellurium occur in the same column. Our study of the halogens prepares us to be properly impressed by the placing of chlorine, bromine, iodine, and fluorine in the same group.

The third series beginning with potassium includes two "octaves," potassium to manganese and copper to bromine, and is called a long series. Iron, cobalt, and nickel are transition elements bridging the gap between the two simple "octaves." The fourth and fifth are also long series with transition groups.

The fifteen rare-earth metals, with a usual valence number of three, occur together in monazite sand and are hard to separate.

The Rare Earths. The rare earths (57-71), a unique series of comparatively rare elements found as oxides in the earth, usually have a valence number of three but they may form ions with charges of 2^+ , 3^+ , 4^+ , or 5^+ . They are very difficult to separate from each other because their atomic radii are nearly equal (as well as their atomic volumes) and their chemical properties are similar.

Valence Changes. The elements of Group O are so inactive that they have no combining capacity at all, therefore no valence. In Group I all elements are monovalent and their oxides are such as Na_2O or Ag_2O (general formula, R_2O). In Group II the valence increases to two. Their oxides are such as CaO or ZnO (general formula RO). Toward oxygen the maximum valence number of the different groups rises regularly to seven (R_2O_7) but toward hydrogen (or chlorine) the valence number rises only to four (in Group IV) and then falls steadily to one. Chlorine in Group VII is found in Cl_2O_7 and in HCl .

Property Changes. The elements of Group I form strong bases, those of Group II only moderately strong bases; and in the middle groups, III and IV, the hydroxides are weakly basic or even weakly acidic, as in carbonic acid. Remember that most acids as well as all bases are hydroxides. Aluminum hydroxide ionizes both as a weak acid and a weak base — an “amphoteric” electrolyte, as is zinc hydroxide. In Group V the elements form strong acids, such as phosphoric and nitric. Group VI permits the formation of strong acids, such as sulfuric and chromic, and of course Group VII is the source of the halogen acids. At the left the elements are strongly basic, at the right strongly acidic, and in the middle the elements resemble both types.

Meyer was especially interested in the regular, periodic variation in such properties as melting point, density, and malleability. These change in much the same way as basicity and acidity.

There is a steady change of properties vertically as well as horizontally in the table. In any given vertical column density increases from the top to the bottom, as does the metallic or electro-positive character.

Atomic volumes also show periodic changes with increasing atomic weights, the alkali metals being high in their respective periods. By atomic volume we mean the volume occupied by one gram atomic weight, usually in the crystalline form. For sodium it is calculated as

$$\frac{23 \text{ g.}}{0.97 \text{ g./ml. density}} = 23.7 \text{ ml.}$$

PERIODIC TABLE SHOWING ATOMIC NUMBERS IN RED										
PERIOD	GROUP 0	GROUP I	GROUP II	GROUP III	GROUP IV	GROUP V	GROUP VI	GROUP VII	GROUP VIII	
0		1 H 1.008								
I	2 He 4.003	3 Li 6.940	4 Be 9.02	5 B 10.82	6 C 12.01	7 N 14.008	8 O 16.0000	9 F 19.00		
II	10 Ne 20.183	11 Na 22.997	12 Mg 24.32	13 Al 26.97	14 Si 28.06	15 P 30.98	16 S 32.066	17 Cl 35.457		
III	18 A 39.944	19 K 39.096	20 Ca 40.08	21 Sc 45.10	22 Ti 47.90	23 V 50.95	24 Cr 52.01	25 Mn 54.93	26 Fe 55.85	27 Co 58.94
		29 Cu 63.54	30 Zn 65.38	31 Ga 69.72	32 Ge 72.60	33 As 74.91	34 Se 78.96	35 Br 79.916		28 Ni 58.69
IV	36 Kr 83.7	37 Rb 85.48	38 Sr 87.63	39 Y 88.92	40 Zr 91.22	41 Nb 92.91	42 Mo 95.95	43 Tc 99(?)	44 Ru 101.7	45 Rh 102.91
		47 Ag 107.880	48 Cd 112.41	49 In 114.76	50 Sn 118.70	51 Sb 121.76	52 Te 127.61	53 I 126.92		46 Pd 106.7
V	54 Xe 131.3	55 Cs 132.91	56 Ba 137.36	57 La Rare-Earths	72 Hf 178.6	73 Ta 180.88	74 W 183.92	75 Re 186.31	76 Os 190.2	77 Ir 193.1
		79 Au 197.2	80 Hg 200.61	81 Tl 204.39	82 Pb 207.21	83 Bi 209.00	84 Po 210.0	85 At 211(?)		78 Pt 195.23
VI	86 Rn 222	87 Fr 223(?)	88 Ra 226.05	89 Ac 227(?)	90 Th 232.12	91 Pa 231	92 U 238.07			

The rare-earths, Lanthanide Series, are La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu. A similar Actinide Series includes the new 93, 94, 95, 96.

Actinide Series	89 Ac 227(?)	90 Th 232.12	91 Pa 231.	92 U 238.07	93 Np 237(?)	94 Pu 239(?)	95 Am 241(?)	96 Cm 242(?)
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PERIOD	IA	IIA	<div>PERIODIC TABLE OF THE ELEMENTS: ATOMIC WEIGHTS AND ELECTRON CONFIGURATIONS</div> <div>The Electrons in the Three Outer Energy Levels</div> <div>Transitional Elements -</div>							
1 K	1 H 1.008 1									
2 K-L	3 Li 6.940 2-1	4 Be 9.02 2-2								
3 K-L-M	11 Na 22.997 2-8-1	12 Mg 24.32 2-8-2								
			IIIA	IVA	VA	VIA	VIIA	VIII		
4 L-M-N	19 K 39.096 8-8-1	20 Ca 40.08 8-8-2	21 Sc 45.10 8-9-2	22 Ti 47.90 8-10-2	23 Va 50.95 8-11-2	24 Cr 52.01 8-13-1	25 Mn 54.93 8-13-2	26 Fe 55.85 8-14-2	27 Co 58.93 8-14-2	28 Ni 58.71 8-14-2
5 M-N-O	Rb 85.48 18-8-1	Sr 87.63 18-8-2	39 Y 88.92 18-9-2	40 Zr 91.22 18-10-2	41 Cb 92.91 18-12-1	42 Mo 95.95 18-13-1	43 Tc 99. 18-14-1	44 Ru 101.7 18-15-1	45 Rh 101.1 18-15-1	46 Pd 106.4 18-15-1
6 N-O-P	Cs 132.91 18-8-1	Ba 137.36 18-8-2	57-71 La-Lu Rare-Earths	72 Hf 178.6 32-10-2	73 Ta 180.88 32-11-2	74 W 183.92 32-12-2	75 Re 186.31 32-13-2	76 Os 190.2 32-14-2	77 Ir 192.2 32-14-2	78 Pt 195.1 32-14-2
7 O-P-Q	Fr 223? 18-8-1	Ra 226.05 18-8-2	89-96 Ac-Cm Actinide Series							
Lanthanide Series Rare-Earths N-O-P			La 138.92 18-9-2	Ce 140.13 19-9-2	59 Pr 140.92 20-9-2	60 Nd 144.27 21-9-2	61 Pm 147. 22-9-2	62 Sm 150.43 23-9-2	63 Eu 152. 24-9-2	64 Gd 157. 24-9-2
Actinide Series O-P-Q			89 Ac 227. 18-9-2	Th 232.12 19-9-2	91 Pa 231. 20-9-2	92 U 238.07 21-9-2	93 Np 237? 22-9-2	94 Pu 239? 23-9-2	95 Am 243? 24-9-2	96 Cm 247? 24-9-2

TS: ATOMIC NUMBERS IN RED

Energy Levels Are Represented

Elements

					IIIB	IVB	VB	VIB	VIIB	0
										2 He 4.003 2
					5 B 10.82 2-3	6 C 12.010 2-4	7 N 14.008 2-5	8 O 16.0000 2-6	9 F 19.00 2-7	10 Ne 20.183 2-8
					13 Al 26.97 2-8-3	14 Si 28.06 2-8-4	15 P 30.98 2-8-5	16 S 32.066 2-8-6	17 Cl 35.457 2-8-7	18 Ar 39.944 2-8-8
VIII A					IB	IIB				
26 Fe 55.85 8-14-2	27 Co 58.94 8-15-2	28 Ni 58.69 8-16-2	29 Cu 63.54 8-18-1	30 Zn 65.38 8-18-2	31 Ga 69.72 8-18-3	32 Ge 72.60 8-18-4	33 As 74.91 8-18-5	34 Se 78.96 8-18-6	35 Br 79.916 8-18-7	36 Kr 83.7 8-18-8
44 Ru 101.7 18-15-1	45 Rh 102.91 18-16-1	46 Pd 106.7 18-18-0	47 Ag 107.880 18-18-1	48 Cd 112.41 18-18-2	49 In 114.76 18-18-3	50 Sn 118.70 18-18-4	51 Sb 121.76 18-18-5	52 Te 127.61 18-18-6	53 I 126.92 18-18-7	54 Xe 131.3 18-18-8
76 Os 190.2 32-14-2	77 Ir 193.1 32-17-0	78 Pt 195.23 32-17-1	79 Au 197.2 32-18-1	80 Hg 200.61 32-18-2	81 Tl 204.39 32-18-3	82 Pb 207.21 32-18-4	83 Bi 209.00 32-18-5	84 Po 210. 32-18-6	85 At 211. 32-18-7	86 Rn 222. 32-18-8
62 Sm 150.43 23-9-2	63 Eu 152.0 24-9-2	64 Gd 156.9 25-9-2	65 Tb 159.2 26-9-2	66 Dy 162.46 27-9-2	67 Ho 164.94 28-9-2	68 Er 167.2 29-9-2	69 Tm 169.4 30-9-2	70 Yb 173.04 31-9-2	71 Lu 174.99 32-9-2	
94 Pu 239? 23-9-2	95 Am 241? 24-9-2	96 Cm 242? 25-9-2								

The Rare Gases. Mendeleeff knew nothing of Group O. When these six elements were discovered they fitted in very well as a transition group connecting the extremely acidic elements of Group VII with the extremely basic elements of Group I. Since they are completely inactive, they have no valence and form no compounds.

Sub-groups. Below sodium in Group I we observe that copper, silver, and gold resemble the rest of the family mainly in valence number, but resemble each other in several other ways. In Group II the zinc, cadmium, and mercury make a good family, but are not remarkably like barium, calcium, and strontium. In Group VII manganese has little relation to the halogens but it does form certain compounds of similar formula, for example, KClO_4 and KMnO_4 . So each column is divided into two sub-groups, A and B, often written at the two sides of the column.

The queer position of iron, nickel, and cobalt (queer in consideration of their valence numbers) is explained by J. J. Thomson as an example of an increase in the positive charges of the atomic nucleus by one without the occurrence of an additional valence electron in the *outer* shell of the neutral atom. This additional compensating electron went into an *inner* shell. Thus atomic weight increased while valence number did not.

Defects of the Mendeleeff Periodic System. It is difficult to place hydrogen in this system, but it is usually written in Group I because of its valence and the fact that it becomes a positive ion.

Tellurium is next heavier than iodine, and yet if placed in this order iodine would not be grouped with chlorine, bromine, and fluorine where it belongs, nor would tellurium be listed in the company of sulfur and selenium. The temptation to change places, thus putting these two elements where certain properties clearly indicate they belong, is irresistible. But, written as they are in all tables, the consecutive order of atomic weights is broken down. Of course many attempts were made to prove that the atomic weights recorded are in error or to show that tellurium is really a compound. All of these failed. Equally annoying is the argon-potassium situation. A glance at the table shows that each

conforms to the rule about "birds of a feather." But another glance at their atomic weights indicates that their places in any regular order have been interchanged.

Exercise

1. An element is discovered with compounds similar to those of manganese. From the analysis of its chloride the equivalent weight is found to be 49.4. What is the atomic weight? Why?

Another weak point is the lack of quantitative relations. Everything is qualitative — the properties change in a general way. And it seems unfortunate that manganese must be grouped with the halogens which it resembles so slightly. There are other examples of ill-matched elements. Furthermore only one valence is considered. The rare earths with a general valence number of three do not seem readily to fit in.

Advantages of the Periodic System. Although we admit the imperfections of the system, we are convinced of the existence of a fundamental relation between properties and atomic weights. The system has been of the greatest service in more ways than one. We place the following to its credit:

1. Classifying Facts. As an aid in classifying a multitude of separate facts it helps the memory and makes for clearness.

2. Predicting New Elements. By its help new elements have been predicted and a few of them were discovered later. In order to place elements where their properties indicate they belong gaps had to be left here and there in the Periodic Table. The assumption was that elements exist (if we could only find them) which occupy the gaps. And from the position of the gaps remarkable predictions as to the properties of the missing elements have been made. Mendeleeff was bold enough to predict the existence of the elements we now know as scandium, gallium, and germanium. In a few years all three were discovered with properties in marvelous agreement with those predicted by Mendeleeff.

Mendeleeff made no predictions about Group O, but after the discovery of argon and helium it was evident to Sir William Ramsay, the English chemist, that there were places for three

more inert gases. As the result of brilliant investigation he discovered three such gases and named them neon, krypton, and xenon. Predictions were completely fulfilled in this instance. There was, however, something yet to be done in filling in the gaps. Mendeleeff predicted an element between molybdenum and ruthenium. He placed it in Group VII and called it eka-manganese. Long afterwards this element was discovered — and named masurium, although in 1947 the name “technetium,” Te, was proposed.

There have been disputed claims of the discovery of elements 85 and 87, finally confirmed by atomic energy research. Element 85 seems to resemble the metals more than the halogens while element 87 resembles the sodium family. The recent creation of elements 93, 94, 95 and 96 is discussed in the chapter on Nuclear Chemistry. These are neptunium, plutonium, americium and curium.

3. Correcting Atomic Weights. The failure of certain elements to fall into the group to which they evidently belong because of their properties has led to very careful redetermination of their atomic weights and in some instances to the discovery of errors. This was notably true of cesium, which had been given an atomic weight of 132.91. The logic of the table indicated that this was surely too low. More accurate work gave us 132.91 as the correct value quite in keeping with the Periodic Law. Mendeleeff insisted that the known atomic weights of uranium and beryllium (glucinum) must be wrong. Later a study of vapor densities of their volatile compounds revealed the predicted errors.

The periodic system has aided in the determination of atomic weights of elements whose compounds are not gaseous. For example, the combining weight of radium indicated possible atomic weights of 113 with RaCl as a correct formula or 226 with RaCl_2 as a correct formula. But radium resembles the divalent calcium and barium rather than monovalent sodium and potassium. Consequently RaCl_2 and an atomic weight of 226 were agreed upon. Of course the Law of Dulong and Petit could have been used in deciding between the possible atomic weights of radium.

Other Classifications of Elements. It is admitted that the periodic grouping of the elements in accordance with their atomic weights is not perfect. These imperfections are removed when the periodic grouping of the elements is based on *atomic numbers* instead of atomic weights.

ATOMIC NUMBERS

It has been known for about fifty years that cathode rays (a stream of electrons) on striking any substance in their path produce the vibrations known as X-rays (see page 25). It was not until 1914 that Moseley, a young English physicist, measured the wave lengths of these rays emanating from different metals used as anti-cathodes in an evacuated X-ray tube. He made each of the metals the target (anti-cathode) in an X-ray bulb. The X-rays were then passed through a thin crystal of potassium ferrocyanide on to a photographic plate. From the photographic spectra secured he calculated the wave lengths. These wave lengths decrease in a regular way with increasing atomic weight. In fact Moseley found a simple numerical relation between the wave lengths of the most intense lines in the different X-ray spectra.

Put briefly, Moseley discovered an almost linear relationship between the characteristic X-ray frequencies and the squares of the atomic numbers for a series of elements. He used one for the atomic number of the lightest element, two for the next heavier, with the others arranged in order of increasing atomic weights.

These *atomic numbers* are all whole numbers. The atomic numbers are approximately half the atomic weights, and represent, in reality, the number of positive charges of electricity (protons) in the nucleus of the atom of each element. In addition to the free protons there are (except in the case of hydrogen) some neutrons.

The atomic numbers 57–71 belong to the metals of the “rare earths,” not listed in the table. All of them (fifteen) belong to the aluminum family. Hafnium with an atomic number of 72 has been discovered since Moseley improved the periodic table as have others shown in the Table of Atomic Numbers.

It is evident that this table is superior to the periodic table of Mendeleeff, for the consecutive order is here used for argon and potassium as well as for iodine and tellurium without spoiling the group arrangement by properties. The fundamental character of an element is determined by its nuclear charge more than by its atomic weight.

In the light of these findings the Periodic Law may be reworded with exactness. The chemical properties of the elements are a periodic function of their position in a series determined by their X-ray spectra. Or, more briefly, *the chemical properties of the elements are a periodic function of their atomic numbers.*

The long form of the Periodic Table is found inside the back cover. Compare it with Mendeleeff's short form.

The modern table of atomic numbers with long periods has a number of advantages over the older Mendeleeff table (short form). In the older form the placing of the subgroups and main groups in a single column was confusing and annoying. In the long form the "transitional elements" stand out with clear emphasis.

Some Properties of the Transitional Elements¹

1. In the transitional elements the outer electron shell and the one next to it are incompletely filled while in the rare earth elements there are three incomplete electron shells. The normal elements have only one incomplete shell (the outer or valence layer), with the few exceptions of the inert gases.

2. One of the outstanding characteristics of the transitional elements is their variable valence numbers.

3. In any one period the properties of the transitional elements depend largely upon the state of oxidation because the ions in that period are of nearly the same size. With normal elements great changes in properties within the period may occur as in passing from sodium to chlorine.

4. Variations in valence number, if any, occur in *two* steps with the normal elements but in only *one* step with the transitional elements.

¹ Adapted from L. S. Foster, *J. Chem. Ed.*, 409 (1939).

5. Only the transitional and rare-earth elements can form simple ions which are colored, due to the influence of an incomplete inner electron shell. But they can not form true hydrides such as CH_4 and NaH . On the other hand they are the only elements that form volatile carbonyls, as $\text{Ni}(\text{CO})_4$.

6. These transitional elements are gray-white metals, often of unusual hardness, ductility, tensile strength, malleability and electrical conductivity. The elements with highest density, melting point and boiling point are, in general, found in this group.

Hydrides. Binary compounds with hydrogen, such as NaH , are formed by the elements of IA, IIA, IIIB, IVB, VB, VIB, VIIB only. Elements of Group VIII may take up hydrogen but not in stoichiometric (compound-forming) proportions.

Exercises

2. The discovery of Element No. 87 gives us an opportunity to predict its properties. What do you think will be its density, melting point, boiling point, action on water, color of its hydroxide, chloride, and sulfate, properties of its carbonate and hydroxide? You will already have the following items in mind:

ELEMENT	DENSITY	MELTING POINT	BOILING POINT
Li	0.534	186°	1200°
Na	0.971	97.5°	880°
K	0.862	62.3°	760°
Rb	1.532	38.5°	700°
Cs	1.90	28.5°	670°

3. What are some outstanding properties of the "transitional" elements?

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Chapter 27 RADIOACTIVITY. STRUCTURE OF THE ATOM

RADIOACTIVITY

X-Rays. Röntgen, in 1895, observed mysterious radiations, "X-rays," proceeding from Crookes electric discharge tubes (high vacua) and penetrating supposedly opaque substances such as paper, wood, flesh, and fabrics. These rays were secondary, that is, they were started by the impact of cathode rays on glass or other substance in their path. The fact that bones, metals, compounds of such heavy elements as barium, lead and iodine, and certain other substances are opaque to the X-rays makes possible photographs of great use. For example, a needle or bullet can be located in the flesh.

It was at McGill University that the first surgical X-ray photograph was taken, two months after Röntgen announced his discovery in 1895.



Fig. 97. One of the first X-ray photographs, 1896.

X-ray photographs are taken of every weld in oil-cracking stills and were taken of every inch of the many miles of pipe in Boulder Dam. The X-ray device has become a super-microscope peering through several inches of steel for inner flaws or detecting nails in tires. The X-ray has gone into business.

Upon electronic bombardment it is the disturbance of the two electrons in the K energy level, or innermost orbit, of an atom that causes radiation of X-rays, characteristic of the individual element. If the nucleus is heavy, with a large positive charge holding this pair of electrons very strongly, the X-ray waves are shorter than those from atoms with lighter nuclei.

In the Coolidge X-ray tube such a high vacuum is secured that positive ions play no part in the operation. Until the cathode is electrically heated in order to

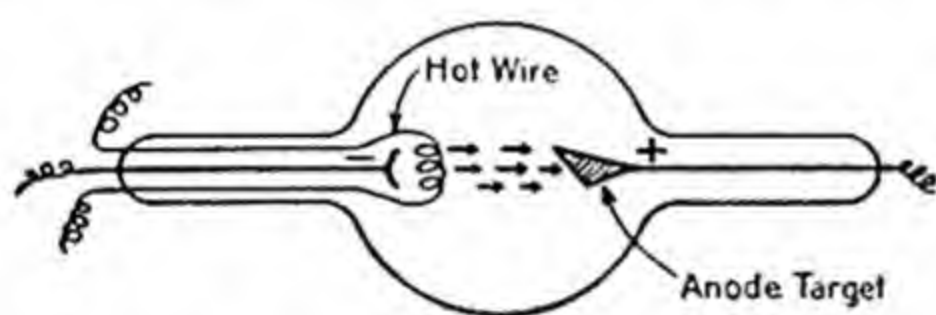


Fig. 98. The Coolidge X-ray tube increases the stream of electrons flying from the cathode as "cathode rays" by raising the temperature of the cathode with an extra heating circuit. Upon impact with the target X-rays are radiated.

"bake electrons out" of the metal the tube shows no conductance, even at 100,000 volts. In operation there is no fluorescence of the glass, therefore but little waste and annoyance from X-rays emanating from glass instead of target.

New X-ray tubes operating at one or two million volts have been made. They can take a photograph through eight inches of steel in three and a half minutes as compared to previous exposures of four and a half hours.

Becquerel Rays. Henri Becquerel in 1896 conceived the idea that perhaps fluorescent substances (those substances that glow in the dark after exposure to light) might be a source of similar penetrating rays. He wrapped photographic plates in black paper and laid them in a dark drawer with a uranium compound and other fluorescent substances. Only the uranium compound produced any effect on the photographic plate. From this beginning Becquerel proceeded to show that any uranium compound gave off these penetrating "Becquerel rays" and that the rays discharged the metallic leaves of an electroscope. Later, Rutherford showed that this was due to ionization of air molecules

surrounding the leaves. With the electroscope one billionth of a gram of radium can be detected.

Radium. Because of Becquerel's work with the penetrating radiations from uranium compounds the Curies (Madame Marie and her husband, Professor Pierre Curie of the Sorbonne) decided in 1896 to examine some of the residues from pitchblende, a uranium mineral, after all the uranium had been extracted. They found that these residues gave off similar but more powerful radiations than the uranium salt itself.

"Their next task was to separate the elements or compounds that had this property. By the ordinary methods of chemical analysis they separated the various elements found in pitchblende residues and tested each for radioactivity, or Becquerel radiations, as it then was called. Most of the elements separated showed no activity.

"However, when bismuth was reached in the analysis it was found that it was intensely active. But since ordinary bismuth or bismuth compounds produced no radiations of this kind it was assumed that a new element closely associated with it in chemical properties had been separated with it. The active substance of the bismuth precipitate was separated, and this was named *polonium* by Madame Curie after her mother country, Poland. This was the first of the radium series to be discovered (1898). Again as the barium was separated, this was found to be intensely active, and as ordinary barium compounds or minerals do not possess this property it was concluded that another element similar to barium had been separated with it at this stage. And by separating this active material from the barium compound a new element was discovered, but not isolated, in 1898, possessing an activity at least 1,000,000 times that of uranium. This was the new element — *radium*." By 1902 Madame Curie had prepared 100 mg. of very pure radium bromide.

In 1910 Madame Curie completed her brilliant work by isolating the element radium. She electrolyzed an aqueous solution of radium bromide, using a mercury cathode. The radium deposited in the mercury was secured by distilling off the latter metal. The radium prepared looked like metallic calcium or

barium and acted like them. It quickly tarnished in the air and decomposed water at a moderate speed. Its carbonate and sulfate were insoluble and its hydroxide a moderately strong base. In short, radium had to be placed in Group II of the Periodic Table. Its valence number in its compounds is 2.

To find the exact atomic weight of radium was a simple matter when the element was known to be divalent. Analysis of the chloride showed the proportion by weight of chlorine and radium to be 35.46 : 113; therefore, the formula must be RaCl_2 and the atomic weight of radium 226.

Madame Curie began her career at the Sorbonne in Paris by washing beakers and bottles, like the youthful Faraday at the Royal Institution in London.

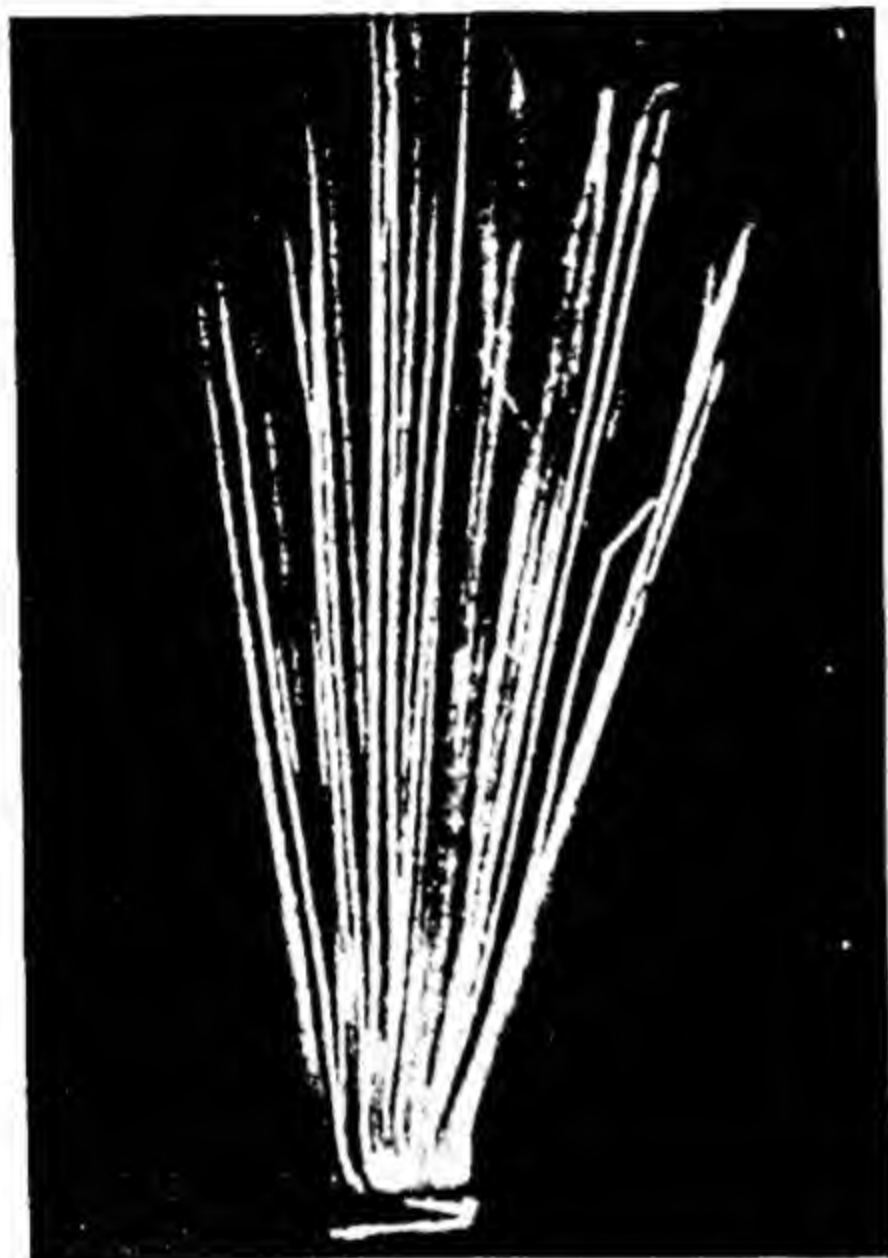


Fig. 99. Fog tracks of alpha particles from radioactive elements crashing through nitrogen. One direct hit on a nitrogen nucleus is shown. (Harkins.)

Radium Rays. Soon after the discovery of radium it was discovered that radium gives off three types of radiations. The *alpha rays* are positively charged atoms (nuclei) of *helium* moving at the rate of 12,000 miles per second. They do not actually travel 12,000 miles, however, in any time; they are stopped com-

pletely before they have gone 8 cm. through the surrounding air. After colliding with several thousand air molecules their initial velocity is reduced to nothing. But they produce very appreciable effects while traveling. Much heat is developed and as they smash through about 200,000 air molecules some of the latter have electrons knocked out of them and thus become ionized particles. Now ionized gas molecules act as nuclei for the condensation of moisture just as well as do dust particles. C. T. R. Wilson showed

this very cleverly by placing a bit of radium in a bulb of air saturated with water vapor. On sudden cooling, the drops of moisture condensed as fog wherever ionized air molecules existed. Wilson photographed these fog tracks, thus showing the path of an alpha particle. This experiment furnished convincing evidence of the existence of atoms and molecules.

The collision between an alpha particle and a crystal of zinc sulfide is marked by a visible flash of light. The *spinthariscopes* (Fig. 100) is a simple contrivance for magnifying this effect. At one end of a small tube is a zinc sulfide screen and near this

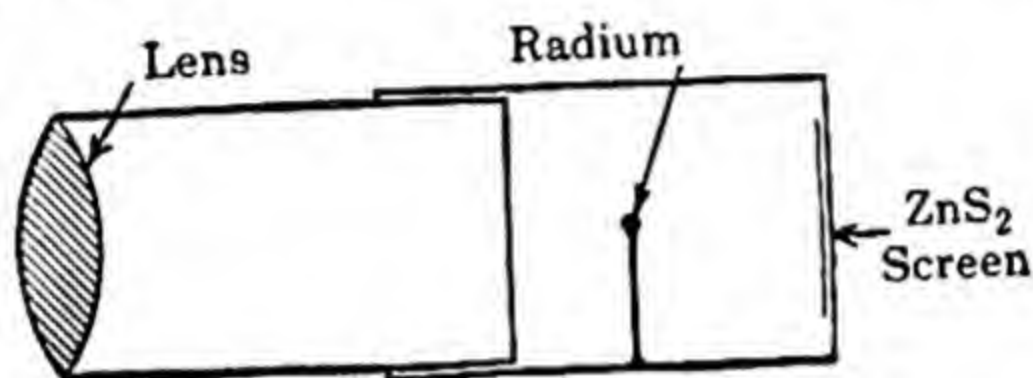


Fig. 100. The spinthariscopes.

is a minute speck of a radium salt. At the other end of the tube is a lens to magnify the flash of light when an alpha particle hits the screen. The human eye needs fifteen or twenty seconds of rest in darkness before it can observe the faint flashes of light. It is decidedly impressive to see the work of a single atom and to realize that this bombardment continues for thousands of years. These alpha rays are able to decompose water, to convert oxygen into ozone, and to bring about the union of hydrogen and chlorine.

The *beta rays* are identical with cathode rays, but move faster and are 100 times as penetrating. These cathode radiations and beta rays are known to be merely streams of electrons. When thrown off by radium they move nearly 186,000 miles per second (the velocity of light). Since they have only $\frac{1}{1836}$ the mass of alpha particles, they are deflected much more by a magnetic field (Fig. 101). As negative particles they are deflected in the opposite direction from alpha particles. In spite of their tremendous initial velocity, they are completely absorbed after smashing through 1 cm. of water or 1 mm. of lead or 4 mm. of aluminum and causing some ionization of atoms.

The *gamma rays* resemble X-rays but are far more penetrating. They are electromagnetic disturbances, not streams of small particles, and hence are not deflected in a magnetic field. Alpha particles are stopped by 0.1 mm. thickness of aluminum foil, beta rays by 10 mm. thickness, and gamma rays by 1 ft. of iron.

The Disintegration of Radium. Rutherford (then at McGill University) was the first to suggest (1902) that radium actually breaks down by throwing off other elements at great velocity.

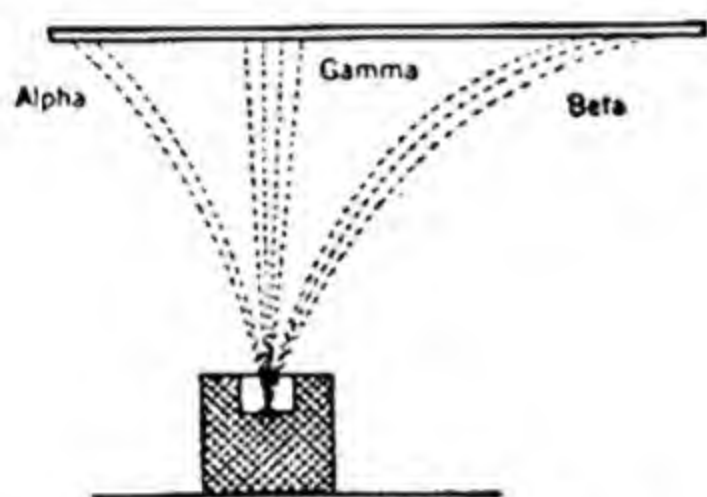


Fig. 101. Three types of radium radiations in a magnetic field.

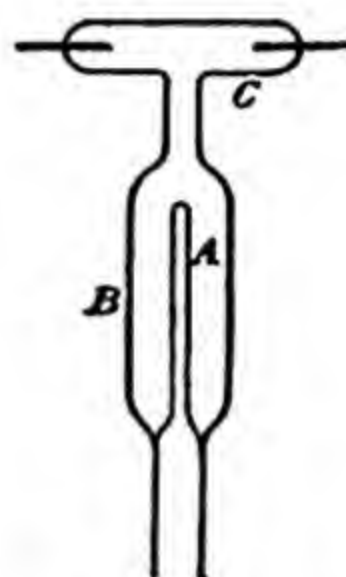


Fig. 102. Detecting the transformation of radon into helium.

Ramsay and Soddy proved that the alpha particles are atomic nuclei of helium. Rutherford later secured a gas from radium which he condensed to a liquid by cooling in liquid air. It then volatilized on warming. This peculiar gas was itself radioactive, although half of this activity disappeared in 3.8 days. It was called "radium emanation" until Ramsay, working with a few cubic millimeters, determined its molecular weight (222.4) and named it *nilon*, now *radon*.

A series of disintegration products has been discovered starting with uranium and, through twelve intermediate products, ending with lead. Since all uranium compounds or minerals are radioactive, they must contain radium. One gram of radium in one year gives off 167 cu. mm. of *helium* gas. By counting the number of alpha particles emitted per second from a minute portion of radium (containing a known number of radium atoms) it has been estimated that half of the radium atoms will have decayed in about 1590 years.

One gram of radium emits 3.7×10^{10} alpha particles per second. Polonium is far more active.

The first definitely established example of transmutation of one element into another was observed and tested by Rutherford in 1909. Using the glass apparatus represented by Figure 102, he evacuated the tubes *B* and *C* and filled *A* with helium under slight pressure. No spectroscopic trace of helium could be observed in *C* during an electric discharge between the two wires. This proved that helium could not leak through the tube *A*. This inner tube *A* was made from glass less than 0.01 millimeter in thickness, so that alpha particles could penetrate it, if given opportunity. Having tested for leaks, Rutherford now filled *A* with radon, the gaseous emanation from radium. In a few hours the spectrum of helium was observed in *C*.

All the radium in the world today is younger than the human race. The half-life of radium is 1590 years. Half of the remainder decays in another 1590 years, and so on. In the radium disintegration series below, He represents an escaping helium nucleus and E an electron. The half-life, atomic weight, and atomic number of each element are given. Small decimal fractions are omitted.

If the nucleus of a radium atom loses a helium atom with two positive charges on it, the atomic number is decreased by two (positive charge decreased by two) and the new element is shifted two groups to the left in the Periodic Table. When Radium B loses an electron from the nucleus, the resulting element is shifted one place to the right because expulsion of an electron from a neutron in the nucleus creates one additional free proton there. These are illustrations of the radioactive displacement law. In radioactive decay the electrons thrown off explosively come from the nucleus (perhaps from explosion of neutrons), not from the energy levels around it.

It is a startling fact that lead occurring in uranium ores has an atomic weight of 206, while common lead with an atomic weight of 207.21 is a mixture of isotopes. To add to the anomaly the atomic weight of lead associated with thorium (also radioactive) is 208.4, a mixture of isotopes. Remember that the weight of an electron is negligible, only $\frac{1}{1837}$ that of a hydrogen atom, and that a helium atom has a weight of 4. Now check the weights in

the uranium-radium-lead series above and it will be apparent that the final product, lead, must have an atomic weight of 206 rather than 207.21. Extremely accurate atomic weight deter-

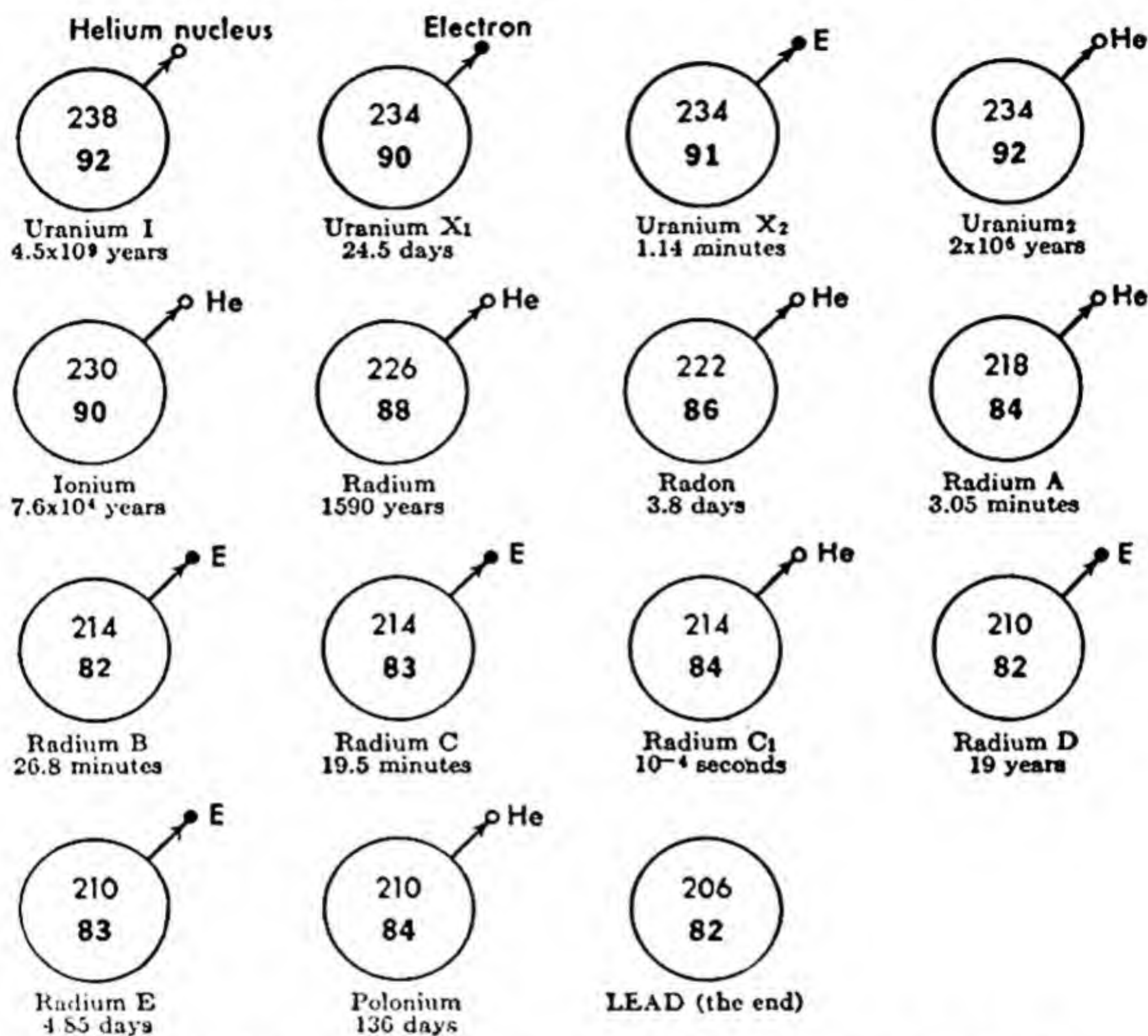


Fig. 103. Disintegration of elements in the radium series. Half-life.

minations by Richards of Harvard gave the same result. Different forms of lead, with identical chemical properties and different atomic weights, are called *isotopes*. The outer electron layer of one lead isotope is the same as that of another.

A beautiful demonstration of the disintegration of radon is possible if an evacuated glass vessel containing a loosely crumpled sheet of paper which has been dusted with phosphorescent zinc sulfide is connected with a small tube of radon gas. On opening the stopcock between the two vessels the radon suddenly fills the large vessel, bombards the zinc sulfide with the high-speed alpha particles of disintegration and causes an astonishing phosphorescent glow, very effective in a darkened room.

Energy of Radium. One gram of radium gives off more than enough heat to melt its own weight of ice every hour: to be exact, 120 cal. This heat is the result of the collisions of alpha and beta particles with surrounding substances. During its full decay life 2,000,000,000 cal. are released as compared with 7870 cal. in the combustion of 1 g. of carbon.

The Radioactive Clock. It is obvious that the minimum age of a uranium mineral may be roughly estimated from the fact that one gram of uranium yields one milliliter of helium in 9,000,000 years. From such calculations and the determination of the ratio of the end-product, lead, to uranium, it is generally believed that the age of the earth is two or three billion years.

Uses of Radium. The chief use of radium today is as a therapeutic agent. Its radiations have a greater effect on unhealthy tissue than on normal tissue, and so, if properly managed, it is possible to destroy cancerous tissue *on the surface* of the body and to relieve pain. Penetrating X-rays can also be used for cancer treatment except where mechanical difficulties intervene. Radium emanation is much used in hospitals because it can be applied conveniently in small tubes or needles and its use permits the radium itself to be locked up in a safe or applied to a particular case. More emanation is constantly being formed and it is sound economy to use it.

Too long an exposure to any considerable quantity of radium causes dangerous burns, so the powerful material is kept in thick lead tubes. Glass tubes containing it develop a violet or brown color. Some gems are affected.

Most radium is converted into the insoluble sulfate to prevent loss from possible water contact in handling.

A luminous paint is prepared for *radiolite* watch faces, door numbers, etc., by mixing 100,000 parts of phosphorescent zinc sulfide with from 1 to 10 parts of a radioactive salt. The action is the same as in the spinthariscopes. About 15 cents' worth is used on a single watch.

Polonium is used in a new auto spark plug to ionize the air, making an easier path for the spark. Polonium decays more rapidly than radium.

Far more important than its use in therapeutics is the light that radioactivity has thrown upon the problems of the constitution of matter.

The Radium Industry. The original pitchblende deposit in Austria was soon exhausted. Fortunately a richer ore was discovered in the Belgian Congo, and carnotite (another uranium mineral) in Utah. In 1931 a rich pitchblende deposit was found north of the Arctic Circle along Great Bear Lake, Canada. The world's stock of radium now approaches a kilogram and the price has fallen from \$135,000 per gram to \$20,000.

One giant X-ray tube can produce more high-power gamma radiation than all the available radium in the world.

Other Radioactive Elements. Thorium decays and yields a series of active products. With ten intermediate products it gives an end-product of lead. The first product, mesothorium, is used as a cheaper substitute for radium. Unfortunately half the material decays in 6.7 years and half of the remainder in another 6.7 years, and so on to the end. The gamma rays from thorium D are the most penetrating known, passing through 16 cm. of lead before being reduced to $\frac{1}{256}$ their potency. Mesothorium decays at least 250 times faster than radium and hence in the pure state is more active than radium. *Actinium* and *polonium* are also radioactive. Many isotopes of common elements, formed by the cyclotron or the atomic pile, are radioactive.

A. V. Grosse in 1934 isolated protactinium (Pa), listed in the Periodic Table to date as U-X, or element No. 91, and has determined its atomic weight as 231 ± 0.5 . It has an average life of 46,000 years and so comes into the laboratory for use. Many of its compounds have already been prepared. Like radium it is a member of a decay series.

STRUCTURE OF THE ATOM

The modern theories of atomic structure were developed after the facts of radioactivity became established — and in the light of these facts.

To Rutherford we owe the first suggestion of the accepted nuclear theory. According to this theory the neutral atom is a miniature solar system with a definite number of positive charges (protons) rather closely compacted in a central nucleus. Asso-

ciated with the protons in the nucleus are neutral particles of proton mass (neutrons). Surrounding the nucleus at relatively great distances are electrons exactly equal in number to the excess of positive charges in the nucleus; hence the neutrality of such an atom.

In nuclei the neutrons may play the role of a binding cement which holds the entire nucleus together, in spite of the strong repulsive force between the positive protons.

Rutherford in 1912, by a study of the scattering of alpha particles shot through a thin film of gold, demonstrated that the positive nucleus of the atom must be small, and surrounded by electrons relatively great distances apart. See Fig. 104.

Gilbert N. Lewis in 1916 advanced his startling "*octet*" theory, which in 1918 and later was so brilliantly applied and extended by *Langmuir*.¹ According to *Lewis*, electrons are arranged around the nucleus in concentric shells. In the rare gases (excepting helium) the outer shell contains eight electrons — and the atom is absolutely inactive chemically.

With increasing atomic weight (due largely to increase in the protons and neutrons of the nucleus) new outer shells are built up around the structure of the atom. Helium has a nucleus of two free protons and two neutrons, and an outer shell of a *stable pair* of electrons. From this element we advance to lithium by increasing the weight of the helium nucleus and surrounding the helium atom with an outer shell with places for eight outer electrons, but with only one such place occupied.

The next heavier element, beryllium, is built up by addition of

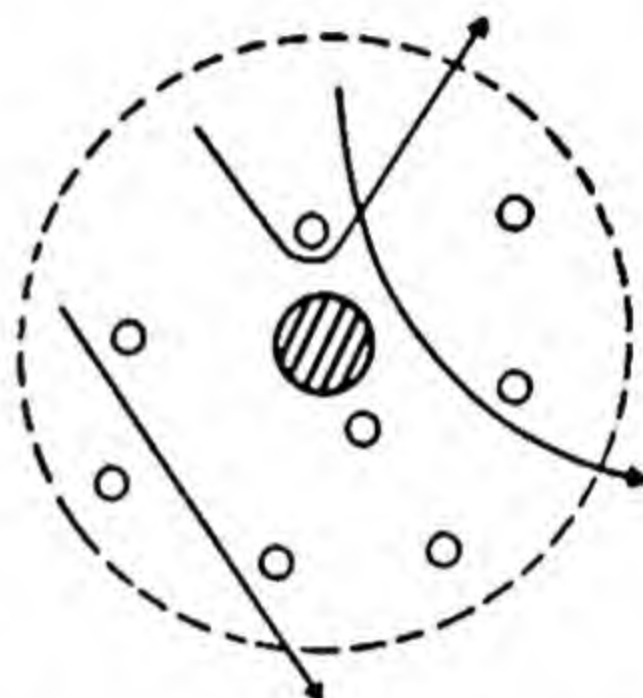


Fig. 104. Positive alpha particles passing through an atom may be uninterrupted if relatively far from the positive nucleus, deflected if near, and reflected back if about to collide with the nucleus.

¹ *Langmuir* held that some outer shells are complete with 18 or 32 electrons so arranged as to give great stability. At this stage it is not essential that we consider anything more than the simplest form of the octet theory.

a second electron to the same outer shell of lithium with the appropriate increase in the nucleus. With the next elements in order of increasing atomic weight — boron, carbon, nitrogen, oxygen, fluorine, and neon — we find a steady increase of electrons in the outer shell until with neon (inactive) the shell is complete with eight electrons — an octet.

Then another shell is added (incomplete) with one electron actually in place (but room for seven more) to form the atom of sodium. This shell may be gradually filled with electrons until with completion of its quota (eight) the atom of argon (inactive) is formed. Thus we see the periodic formation and filling in of outer shells, eight elements in each period building up from one to eight electrons for the outer octet.

We may call the electrons of an incomplete outer shell “valence electrons.” Chemical reaction is merely a matter of *transfer* or *sharing* of these *electrons*. The preponderating tendency of each atom is toward an arrangement of electrons with eight in the outer shell, secured by gain or loss of electrons, or by electron sharing.

The Bohr Atom. Bohr’s conception of the atom (1913), a conception that is *changing under constructive criticism*, differs from the static arrangement of electrons suggested by G. N. Lewis and

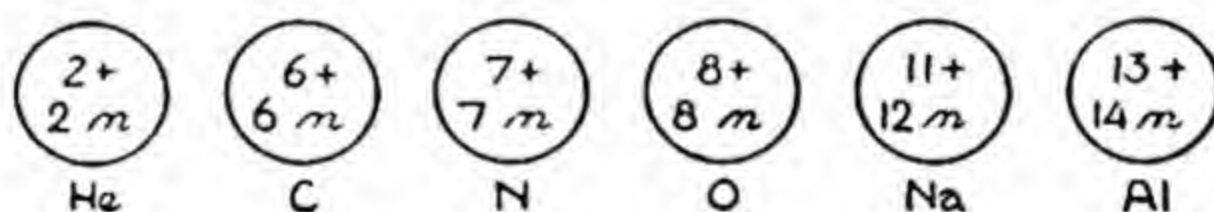


Fig. 105. Atomic nuclei representing “free” protons and neutrons, definite building bricks of matter. The neutrons have the mass of protons but no charge. There is no significance in the fact that in the first four nuclei above the protons are numerically equal to the neutrons.

Langmuir. Bohr held that the planetary electrons revolve at high velocities in circular and elliptical orbits around the nucleus. Sommerfeld in 1919 added the conception of sub-levels. With the heavier atoms the arrangement of orbits is amazingly complicated and it has been suggested that the electrons are spinning as well as revolving around the nucleus and that the nucleus also may be spinning.

There is one distinct advantage in the modified Bohr theory that is worthy of mention here. By the Lewis and Langmuir theory no outer shell can be begun until the electron layers or shells beneath are complete. Not so with the Bohr theory.

There can be only two electrons in the energy level nearest the nucleus, eight in the next layer, and room for more in the layers farther out as represented in uranium — 2, 8, 18, 32, 21, 9, 2, but no element with more than 4 levels has its three outermost levels filled.

In the outer layer or energy level there may never be more than 8 electrons and never more than 18 in the layer next beneath (although there may be fewer). In colorless cuprous compounds the electron distribution from the center out is 2, 8, 18, 1, while in blue cupric compounds the distribution between energy levels is 2, 8, 17, 2. Since valence relates to electrons in the outermost level only it is seen that cuprous copper is monovalent and cupric copper divalent.

In chromium and in copper there is only a small difference in energy between the two alternative levels possible for outer electrons, so an electron can readily be transferred from one level to

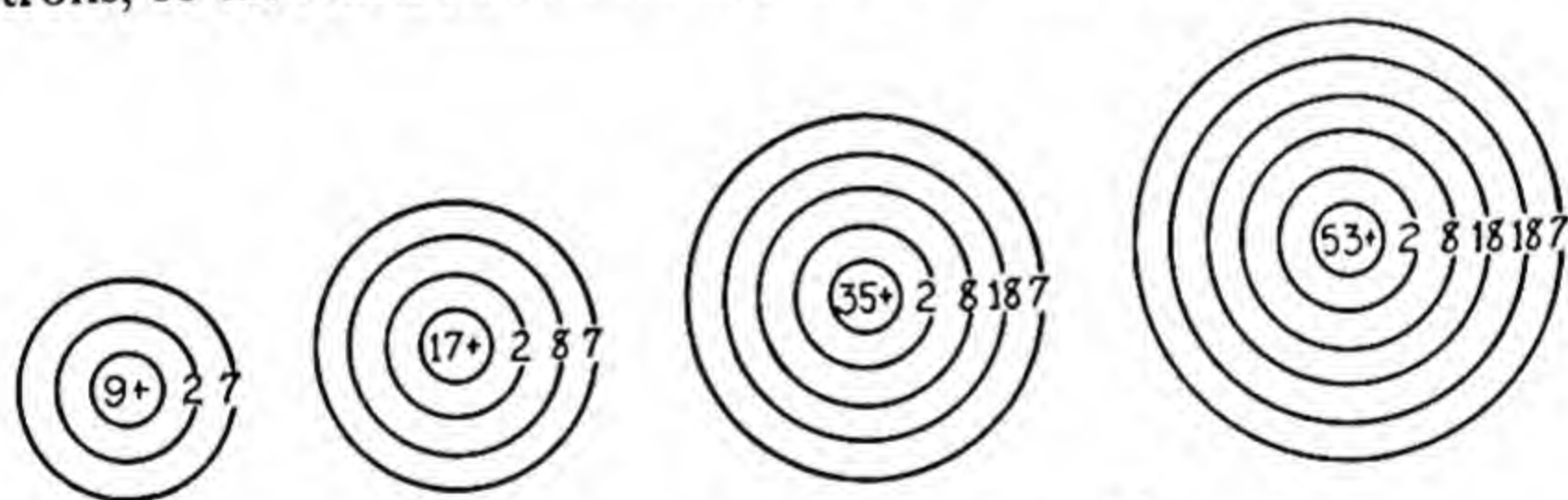


Fig. 106. Bohr orbits of the F, Cl, Br, and I atoms.

the other. Of course an electron dropping from the outermost level to the one beneath is no longer a valence electron.

According to the wave mechanics theory the electrons move in energy pulses like waves, not particles. However, the energy level idea is retained.

On the inside front cover of this book is a table of the elements listing the number of planetary electrons in the various energy levels. The two in the K level next to the positive nucleus are

so powerfully attracted that their displacement causes emission of X-rays. The farther from the nucleus the more readily electrons are displaced by energy from without.

Isotopes. In radium decay some newly created radioactive elements fall into places in the Periodic Table already occupied, that is, they are isotopic forms. The two or more species of any atom differing only in the number of neutrons in the nucleus,

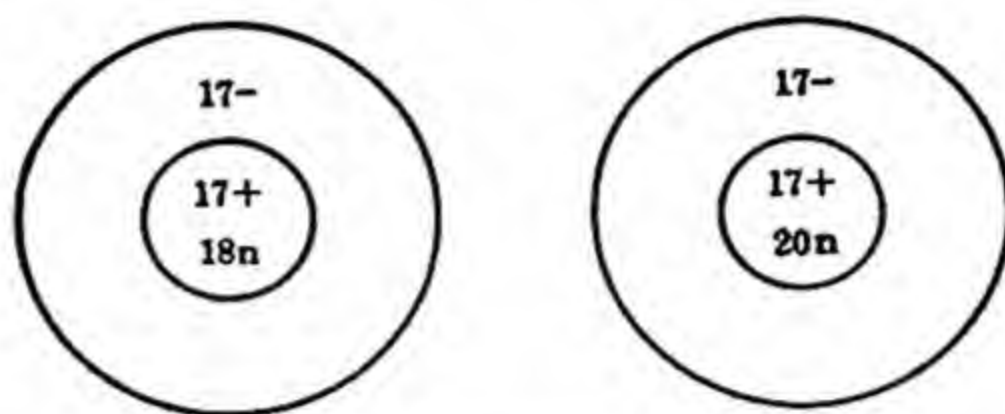


Fig. 107. Isotopes of chlorine.

not in the chemically active outer layer of electrons, are called *isotopes*. Without isotopic forms of an element atomic weights would be whole numbers. For example common chlorine gas consists of chlorine atoms weighing 35 and others weighing 37. The weighted average is 35.47 for about three-fourths of the atoms are the 35 isotope.

In normal carbon 99 out of every 100 atoms have an atomic weight of 12 and one atom has an atomic weight of 13. As shown in the next chapter a radioactive isotope, C^{14} , has been made. Such an isotope can serve as a "tracer" to study how plants transform the atoms of carbon dioxide of the air into their body substance, how organic compounds are created, or how the human body utilizes so many of the carbon compounds of which it is composed.

Positive-Ray Analysis. Mass Spectrometer. In Fig. 108 is represented a vacuum tube (at left) with anode, and a cathode perforated in the center. When a trace of some gas is admitted while a high potential electric discharge takes place the high-speed electrons from the cathode knock electrons out of the gas molecules, thus forming positively charged gas ions. Under the electric stress these positive gas ions are driven toward the cathode, through the small center hole, and on to a photographic

plate. Under the influence of a powerful electrical field and magnetic field, NS, these positive rays are bent out of their straight-line course according to their charge (readily calculated) speed, and mass. Gaseous ions of equal mass are focused on the same line on the photographic plate, those of other masses on parallel lines. Hence it is possible to calculate, from the positions of these bands, relative masses of atoms. Aston, the English

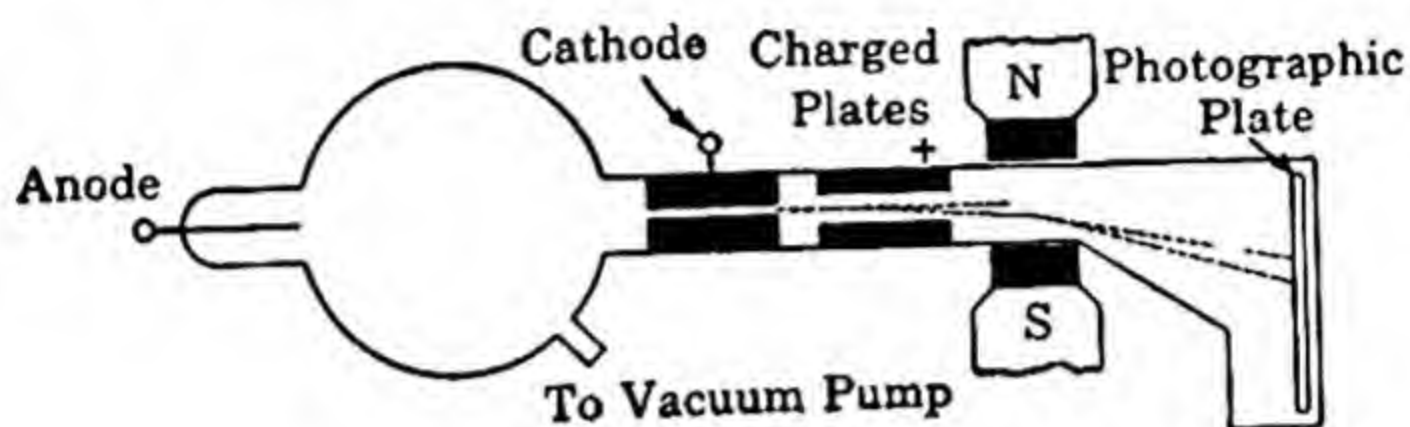


Fig. 108. Positive-ray analysis.

physicist, so improved J. J. Thomson's original apparatus that his error in determining atomic weights was only one part in 10,000. An accuracy of 99,999 parts in 100,000 is possible.

When the rays come from a mixture of isotopes of an element, each isotope is marked by a separate band on the photographic plate. From the position of the band the mass of the corresponding atom can be learned.

With such technique a few hundred isotopes have been detected, and "weighed," for nearly all elements.

The mass spectrometer has become an analytical instrument for gas mixtures. Obviously the gases must be ionized before analysis.

Exercises

1. What are isotopes?
2. What has become of the molecule in a crystal of common salt?
3. What do the outer-shell electrons in an atom have to do with valence? What do they have to do with chemical reactions?
4. What is the difference between the electron processes in formation of CCl_4 and NaCl ?
5. What is the difference between the Bohr atom and the Lewis-Langmuir atom?

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6. What started us on our way to the present conception of the atom?
7. Why doesn't carbon tetrachloride ionize?
8. What is the nature of the neutron?
9. How has the discovery of radioactivity aided pure science? Industry? Medicine?
10. Since it is the positively charged mass of the nucleus of the atom which "holds" or attracts electrons, in which atom will the valence electron be held on to or attracted most strongly, that of lithium or that of rubidium? The lithium electron levels contain 2, 1 electrons while the rubidium levels contain 2, 8, 18, 8, 1.
Give the *REASON* for your answer.
11. In what ways do the X-ray tube and radium compete?

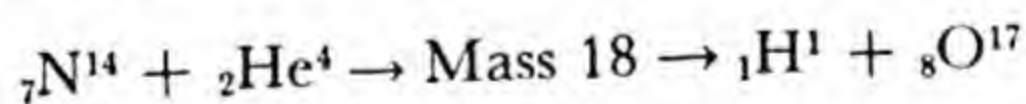
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Chapter 28 NUCLEAR CHEMISTRY

Outer planetary electrons are readily stripped from atoms by heat, ultra-violet light, or the current-passage through a Crookes tube. But when the nuclei of radioactive atoms spontaneously eject particles or when direct hits on a nucleus are made by fast-moving particles of various sorts something more wonderful takes place. The changes produced are those of nuclear chemistry, so deep-seated that they may involve the transmutation of elements.

It was Rutherford, in 1919, who first succeeded in the artificial disintegration of an element, nitrogen, by bombardment with alpha rays (high-speed helium nuclei). In rapid succession he knocked protons (hydrogen nuclei) out of a dozen elements by the same technique:

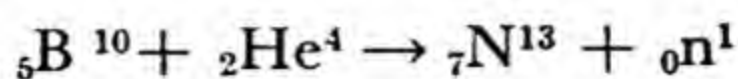


In ${}_7\text{N}^{14}$, for example, the 7 is the atomic number while the 14 represents the mass or atomic weight.

This new isotope of oxygen, supposed to be the product of the above nuclear reaction, was not actually recognized until over a decade later.

In 1931 Chadwick, in England, identified the neutron (represented by "n") as a component of the atomic nucleus. Forced out by bombardment of beryllium with alpha particles it showed penetrative power so great as to be explained only by a lack of charge. The neutron has a mass of one.

In 1934 Irène and Jean Frédéric Curie-Joliot made aluminum, boron, and magnesium radioactive by attacking their nuclei with a stream of alpha particles from polonium:



In this sensational nuclear warfare every conceivable type of bullet was tried, in several instances with brilliant success.

BULLETS FOR ATOM-SMASHING

Alpha Particles: nuclei or positively charged hearts of helium atoms thrown off at high velocity by radium, polonium, mesothorium, and other radioactive elements.

Electrons: the negative beta particles ejected from radioactive elements, from heated substances, and from the cathodes of X-ray tubes or in a stream from the betatron.

Protons: hydrogen nuclei or hearts formed from hydrogen during passage of an electric discharge through a vacuum tube and given high velocity as "canal rays" passing through a hole or canal in the cathode. Other gases in such a tube may be ionized and driven through the cathode canal as positive rays.

Neutrons: penetrating neutral particles of protonic mass ejected from beryllium and certain other elements during bombardment by alpha particles or by high-speed deuterons. They are also secondary products in uranium fission.

Deuterons: nuclei or hearts of deuterium, heavy hydrogen atoms, consisting of a proton and a neutron.

X-rays from the betatron are so powerful that they act like bullets in disrupting nuclei.

Lord Rutherford believed that Nuclear Chemistry or Nuclear Physics is, in a sense, a new branch of knowledge, important to chemist, physicist, biologist, and physician. Now we realize its role in engineering and war.

BULLETS AND MASS

Alpha particle, 4.003
Electron, $\frac{1}{1836}$
Proton, 1.00758

Neutron, 1.00897
Deuteron, 2.01473

ATOM-SMASHING APPARATUS

The earliest device for accelerating the atomic bullets was a giant X-ray tube producing positive rays (canal rays) of any desired gas. Even with high vacuum there is some gas in the tube and it becomes ionized. Tubes operating at one or two million volts are now in use.

Lawrence and his associates at the University of California in 1933 invented the most powerful gun: a cyclotron, in which gaseous ions are given an accelerating tap during rotation by an oscillation of an electrical field. In the original cyclotron a 220-ton magnet is used to hold them in a circular path. Lawrence received the Nobel Prize award in Physics (1939) for this work.

"Voltages produced from high-voltage transformers are applied to hollow metal electrodes shaped like a pill box which has been cut in two and the two halves moved apart a little. This space is evacuated and is provided with a

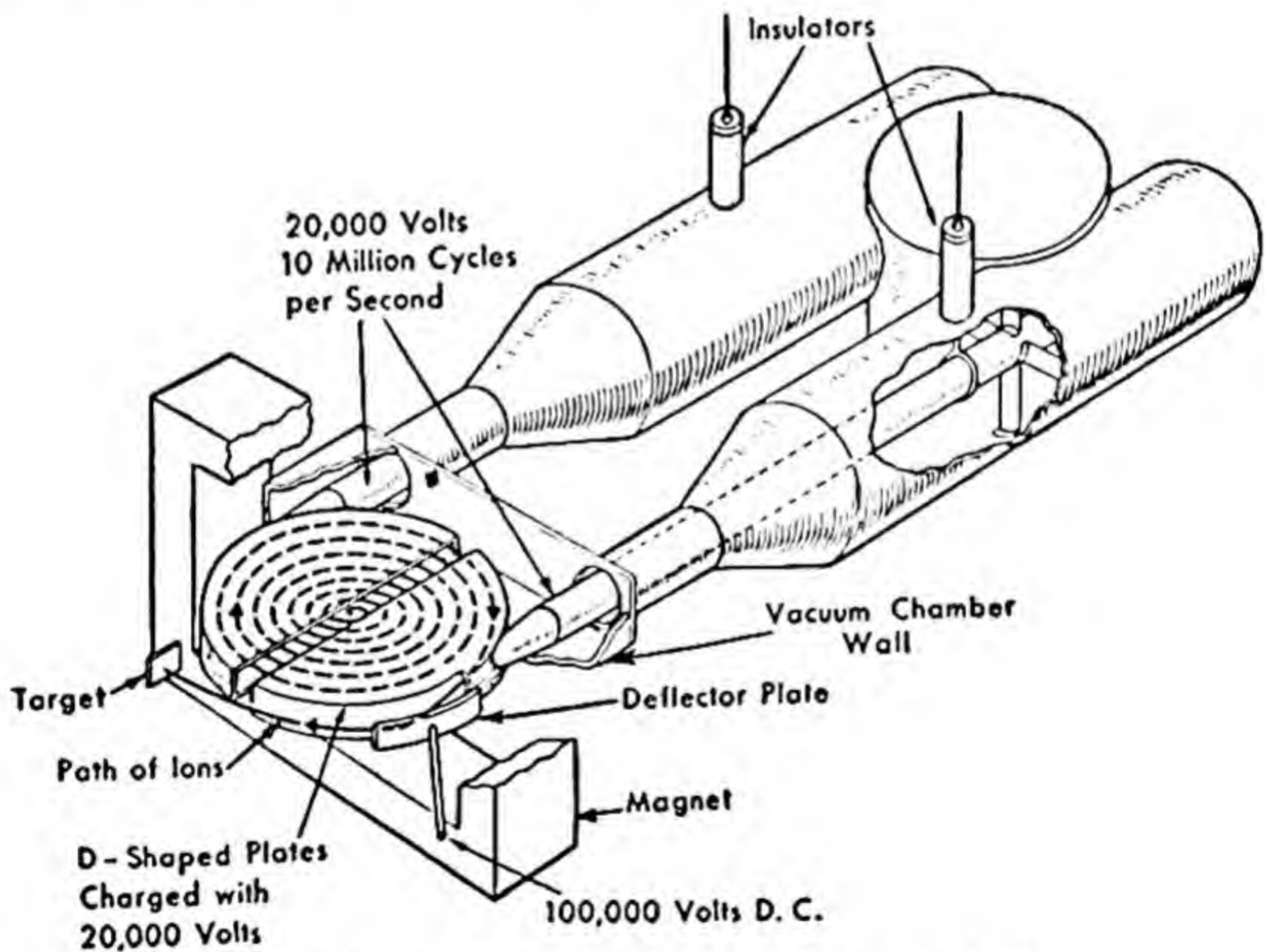


Fig. 109. The cyclotron. (Courtesy *Life* magazine.)

glowing filament against which hydrogen atoms impinge and are converted to hydrogen nuclei. The electrode chambers are subjected to the influence of a powerful magnetic field acting perpendicularly to the path of the particle.

The hydrogen nucleus is attracted into the negative electrode chamber with a speed related to the voltage applied. At the same time its path is depressed by the action of the magnetic field and in a minute fraction of a second the voltage is reversed, giving the hydrogen nucleus another kick equal to the voltage applied. With the current alternating 10 to 20 million times per second, the charged particle moves faster and faster in an ever increasing spiral until it and millions like it are flung out through a tube in the periphery of one electrode as a bombarding beam of charged particles each having a speed corresponding to eight million electron volts. A container of the element to be bombarded is placed in the path of the beam and the effects studied for their information on the structure of the nucleus." (L. A. DuBridge.)

The University of California built a second cyclotron weighing 5000 tons which produces a 200,000,000 electron volt deuteron beam or a 400,000,000 electron volt beam of alpha particles.

A third giant cyclotron is planned to give particles an acceleration of 10,000,000,000 electron volts. In this the circular path of particles would be 110 feet.

With the aid of the cyclotron most elements have been disintegrated. Mercury may thus be converted into gold, at a financial loss! The cyclotron was the most effective device for producing new radioactive substances by atomic disintegration. Now the "atomic pile" has surpassed it. And yet over two thirds of the known elements can be made from uranium by a cyclotron beam of alpha particles.

The Betatron. In this device by Kerst a stream of electrons from a hot filament moves inside a ring-shaped evacuated glass tube supported between the poles of a powerful magnet. These electrons travel around inside the tube 250,000 times in about 0.004 sec., receiving an acceleration at every revolution; then they are released as a beam of beta rays or strike a tungsten target and generate X-rays. The striking speed for one of the largest betatrons of 1946 is 100,000,000 electron volts. Its electromagnet weighs 130 tons. (An electron volt is the kinetic energy of a particle carrying a single electric charge in falling freely through a potential drop of one volt.) The X-rays from this giant betatron are far more powerful than any previously known.

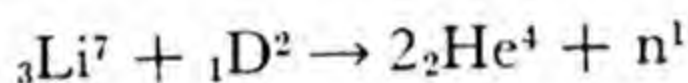
With this betatron's X-ray beam the nucleus of nearly every type of atom has been broken up.

The synchrotron, a modification of the betatron, also promises to become a powerful tool in nuclear chemistry. Synchrocyclotrons are being built.

The linear accelerator now under construction is a straight sectional tube device of power increasing with length. It may rival the cyclotron.

TRANSMUTATIONS

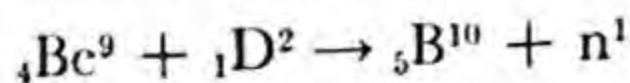
Bombardment by heavy deuterium nuclei, as expected, has proved to be more effective than smashing with hydrogen nuclei. For example, lithium has been transmuted into helium ions or alpha particles by overloading the nucleus so that it breaks apart:



Lawrence in California (1933) forced neutrons out of beryllium by the impact of 3,000,000-volt deuterons. Previously this had been done in Europe by use of alpha-particle bullets. To date not only beryllium but helium, lithium, carbon, argon, nitrogen, oxygen, and other elements have yielded neutrons under bombardment. The neutron is a building brick in atoms.

When a cyclotron beam of heavy hydrogen nuclei, deuterons, moving 25,000 miles per second, strikes beryllium, a copious emission of neutrons is secured. To equal, in this way, the neutron yield of such a cyclotron would require bombardment of beryllium by the alpha particles from 200 pounds of radium. The larger cyclotron may drive alpha particles.

Lauritsen and his associates at the California Institute of Technology found deuterons the most effective atomic bullets for attack on beryllium — if neutrons were desired. Boron is the product of transmutation in this instance:



Speeding alpha particles, protons, or deuterons are probably captured by the nucleus before emission of other units. The new nucleus formed by addition of a proton or other particle is un-

stable and must break down into a stable nucleus, by means of emission of energy or particles, or both.

Ten isotopes of element 43 have been prepared by nuclear reactions from molybdenum. Number 43 (technitium, formerly called masurium) resembles rhenium more closely than it resembles manganese. Volatile oxides and halides have been made and sulfides precipitated by hydrogen sulfide in strongly acid solutions.

Element 61 also has been synthesized by nuclear reactions. Number 85 (astatine) was formed when cyclotron-driven alpha particles bombarded bismuth. It resembles the halogens somewhat but is more metallic than iodine. Number 87, francium, has a half-life of 21 minutes.

In 1944-45 two new transuranium elements, 95, americium (Am) and 96, curium (Cm), were prepared by Seaborg and associates, using cyclotron beams. Later curium was isolated. The preparation of elements 93, neptunium (Np), and 94, plutonium (Pu), is described on the next page.

Uranium Fission. In 1939 and 1940 the atomic "fission" of the uranium isotope of mass 235 by Hahn and Strassmann was recognized both in Europe and in America. This fission

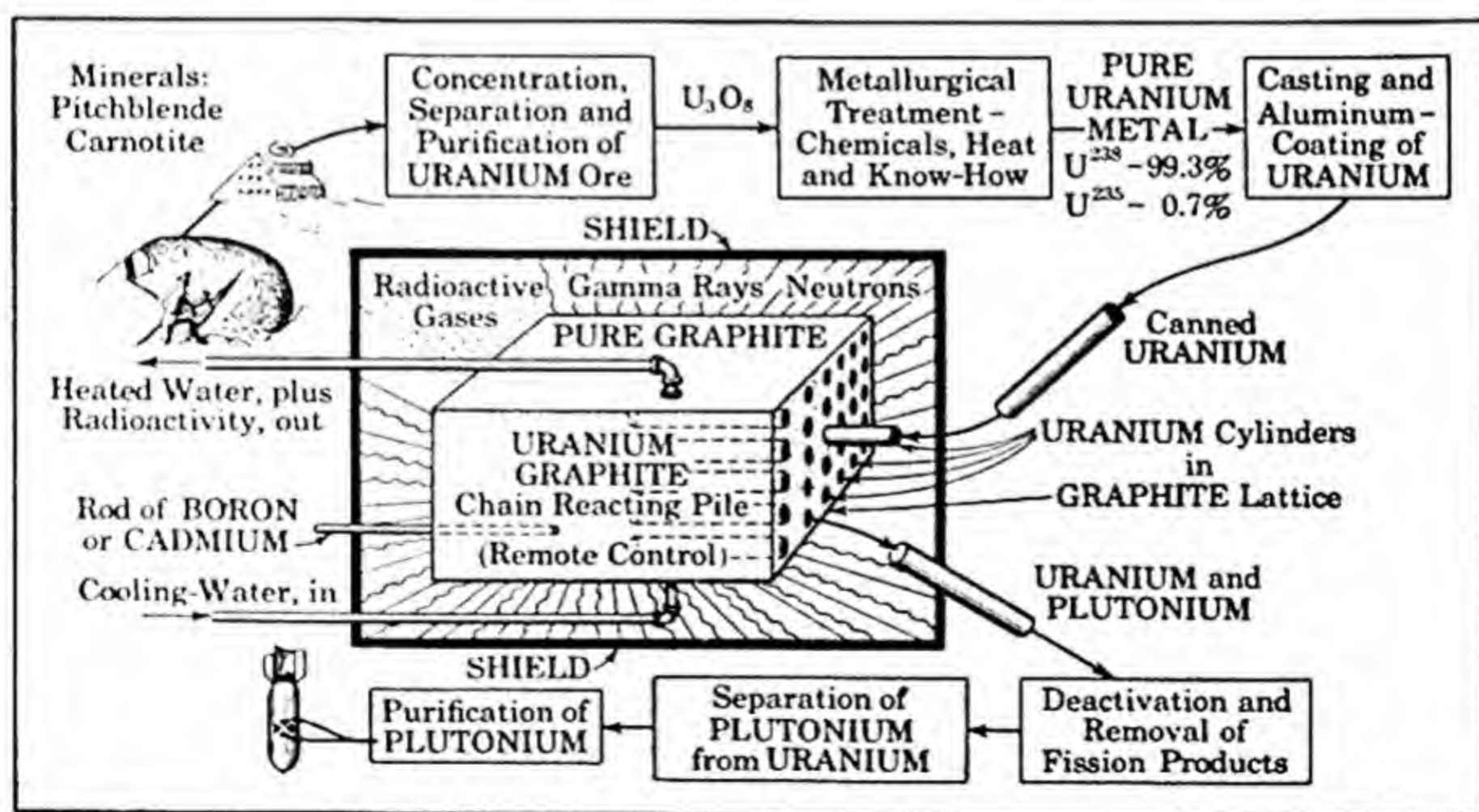


Fig. 110. Uranium pile and production of plutonium. (Courtesy American Petroleum Institute).

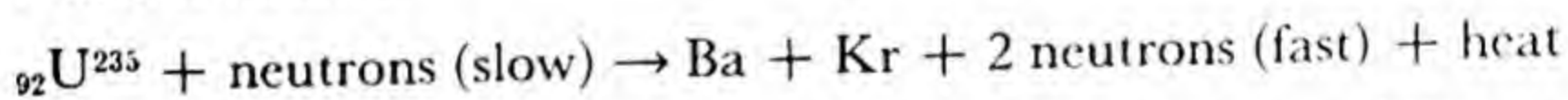
was accompanied by the emission of tremendous energy, nearly 200,000,000 electron volts per atom of U^{235} . Compare this impressive figure with the four electron volts of energy released by burning an atom of carbon or of hydrogen.

There is an important chain of reactions in fission in the sense that secondary neutrons are released to cause other fissions and, theoretically, to continue thus until all the U^{235} in a given sample is exhausted. However, the presence of U^{238} and other impurities quickly breaks this chain reaction. Since U^{235} constitutes only one part in 139 in common uranium the critical problem was separation to obtain pure U^{235} . The problem was solved.

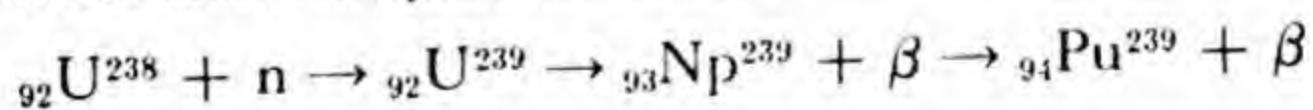
ATOMIC ENERGY AND URANIUM FISSION

Military necessity in atomic bomb research greatly advanced our knowledge of atomic energy — and created four new elements, 93, 94, 95, 96, heavier than any known in nature.

Neutrons from a suitable source were slowed down by passage through graphite or deuterium-rich compounds to the kinetic energy of gas at ordinary temperatures. Slow neutrons are readily captured by the nucleus of the isotope U^{235} . A typical reaction follows:



It was found that the supposedly worthless isotope, ${}_{92}U^{238}$, on bombardment with neutrons became another isotope, ${}_{92}U^{239}$, which in turn soon lost an electron and became a new element, *neptunium* or ${}_{93}Np^{239}$. In a few days this unstable neptunium lost an electron, or beta particle, and became another new and rather stable element, plutonium, ${}_{94}Pu^{239}$.



The next tremendous discovery was that plutonium was fissionable under bombardment by slow or only moderately fast neutrons. It was created on a large scale with many radioactive byproducts and the release of great quantities of energy as heat. The exact method of use of plutonium in the bomb is a military

secret at present. Chemically it is a new element, No. 94, in the table of Atomic Numbers, hence may be separated from the isotopes of uranium and other substances present by chemical means.

The entire chemistry of the planned large-scale separation was worked out with less than 1 mg. of plutonium — a triumph of ultra-microchemistry. Plutonium, 239, has a half-life of 24,000 years.

The uranium isotopes, being chemically alike, are extraordinarily difficult to separate and yet it was accomplished by physical means.

The discovery of plutonium fission multiplied by 100 our previous resources of nuclear energy.

A self-sustaining chain reaction is not possible in a solid block of ordinary uranium metal. The more abundant U^{238} nuclei absorb too many neutrons. Yet if the uranium is cut up into small pieces and these are separated throughout a large block of graphite (a "pile") the neutrons will be slowed down by the graphite so that they can rupture the U^{235} nucleus. Even so if the pile is too small too many neutrons escape from the surface. The danger is that a "critical size" of pile may explode like a bomb. Rods of cadmium or boron are inserted in the pile (by remote control) whenever fission needs to be moderated for safety.

These two elements are unique in their ability to absorb neutrons harmlessly. Of course in an atomic bomb the desired critical size of the mass of U^{235} or Pu^{239} is obtained by suddenly bringing together two lesser masses.

It might be added that fission of a thorium isotope, Th^{232} , by fast neutrons is possible. Elements lighter than mass 210 apparently do not take part in chain reactions although they may be made radioactive. There is great interest in location of new deposits of uranium and thorium minerals.

Until plutonium was found to be fissionable tremendous efforts were made (successfully) to isolate U^{235} . Since the methods used illustrate chemical principles already mentioned in this text they merit attention here. First pure uranium was prepared by electrolysis of KUF_5 in fused $NaCl$ and $CaCl_2$.

1. *Gas Diffusion Method.* According to Graham's Law (p. 69) the rate of diffusion of a gas through a minute hole or an ideal porous barrier is inversely proportional to the square root of its molecular weight; hence molecules of uranium hexafluoride (a gas) containing U^{235} diffuse slightly faster than similar molecules containing U^{238} . A great number of repetitions of the process required acres of porous barriers and thousands of pumps. Uranium hexafluoride, UF_6 , is extremely corrosive so the difficulties were enormous.

2. *Thermal Diffusion Method.* A liquid compound of uranium circulates by convection between two coaxial cylinders maintained at different temperatures. The lighter compound of U^{235} tends to concentrate in the warmer region and that of U^{238} in the cooler region. The enriched output was used as a supply for the electromagnetic separation.

3. *Electromagnetic Method.* The principle of operation is the same as that of the mass spectrograph (p. 312) aided by the cyclotron idea. Molecular ion beams produced by bombarding a gaseous uranium compound, UF_6 , with electrons are accelerated to high velocity in an electric field. The ion beam is then split into two parts by passage through an intense magnetic field, the heavier U^{238} moving in a larger semicircle than the lighter U^{235} .

Recently this principle has been used in analysis of the complex mixture called petroleum. After forced ionization, by electron bombardment, the gas ions follow curved paths with radii proportional to the masses of the particles.

Change of Mass to Energy. If the helium atom with a mass of exactly 4.003 is built up from four hydrogen atoms, there must be a slight loss of mass in the close packing of nuclei since $4 \times 1.008 = 4.032$. Since mass can be converted into energy, the energy released by the sun corresponds to a loss of mass equal to 4,000,000 tons per second.

Put in other terms, when 4.032 g. of hydrogen are converted into 4.003 g. of helium, 700,000,000 cal. are released, while if the same 4.032 g. of hydrogen are burned to form water, only 136,660 cal. are liberated.

Einstein's equation which relates mass and energy is $E = mc^2$ where E is energy, m is mass, and c the velocity of light. A photon (unit particle of light), corresponding to about one million electron volts, would have the mass equivalent to a positron-electron pair. In the fission of enough uranium or plutonium to lose one gram of mass there must be 20 billion calories of heat released as the Einstein equivalent of this loss of mass. When one gram of carbon is burned only 7870 calories are formed.

Atomic Power. In 1946 it was estimated that nuclear power could be produced at a cost of 0.8 cents per kilowatt hour as compared with 0.65 cents for power from coal. In areas far distant from coal fields and, possibly in larger ships, nuclear power may become attractive. Furthermore, its cost may decline as a result of further research. The high temperature of atomic fission is the source of useful power.

CHEMICAL PROPERTIES OF ELEMENTS 93, 94, 95 AND 96

While elements 90 and 91 (thorium and protactinium) show a great chemical resemblance to the first members in the hafnium-to-osmium transition series it is remarkable that 93 and 94 (neptunium and plutonium) show practically no resemblance to rhenium and osmium. Rather they most resemble uranium. Perhaps it is an inner electron shell that is being filled in the progression of elements following uranium.

Seaborg suggests that an "actinide" series beginning with actinium should be written, similar in a sense to the "lanthanide" series that begins with lanthanum.

There are four oxidation states of plutonium, corresponding to positive valence numbers of 3, 4, 5, and 6. A large number of plutonium compounds have been prepared, some of them yielding colored ions.

The lower oxidation states tend to be more stable than is the case with neptunium.

A comparison of the electron shells or energy levels of uranium and plutonium is interesting.

U,	2,	8.18,	32,	21,	9,	2
Pu,	2,	8.18,	32,	24,	9,	2

Like uranium with its uranyl ion, UO_2^{++} (salt forming with anions) plutonium also forms a plutonyl ion, PuO_2^{++} .

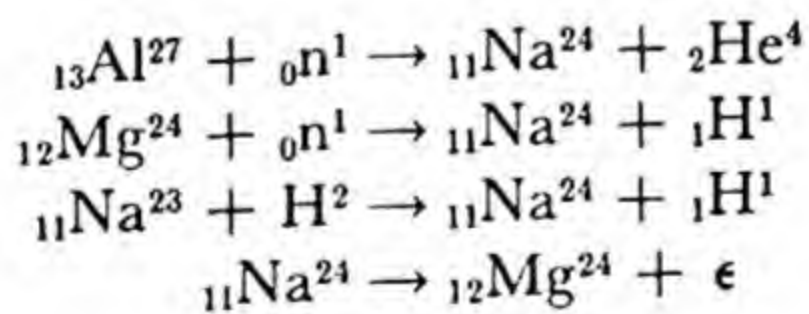
New Elements. Elements 95, Americium, and 96, Curium, were formed by bombarding U^{238} and Pu^{239} with alpha particles from the cyclotron. Neptunium, 93, and Plutonium, 94, have been discussed. Americium has a half-life of 500 years; Curium, only 5 months.

INDUCED RADIOACTIVITY

When induced radioactivity was first produced (1934) by the Curie-Joliot by the bombardment of boron with alpha particles, the disintegration of boron continued for 15 minutes or longer after the bombardment stopped. (See page 316.) With bombarded aluminum the post-bombardment decay period was four minutes.

This extremely important research has been continued in several laboratories with such success that "induced radioactivity" is almost commonplace. Neutron bullets are able to give artificial radioactivity to the nuclei of practically all elements. The atomic pile is now the most powerful source of neutrons. By 1948 at least 500 radioactive isotopes had been produced.

A given kind of radioactive atom can sometimes be made in several ways.



Many elements have two or more radioactive isotopes, such as Al^{26} , Al^{28} , and Al^{29} , produced through different nuclear reactions.

Fluorine has only one stable isotope but three radioactive isotopes, F^{17} , F^{18} , and F^{20} , were made by proton and deuteron bombardment.

Radioactive C^{14} with half-life of 1000 years, has been prepared by neutron bombardment (from the atomic pile) of nitrogen compounds: a transmutation of nitrogen into one of the carbon isotopes. The carbon was captured as carbon dioxide.

Radioactive carbon of atomic weight 14 and long half-life will be valuable as a tracer element in following the course of the reactions by which carbon dioxide is utilized by growing plants (photosynthesis), as well as in the reactions of organic chemistry and biochemistry. It already has great value in industrial research.

When radioactive phosphorus was added to steel it concentrated around blowholes as shown in photographs taken with its own radiations. And the dangerous blowholes were detected.

Temporarily radioactive sodium in common sodium chloride might conceivably be used by physicians for internal radiation.

Compounds of radioactive phosphorus (half-life, 15 days) are being used as tracers in food to find how it is converted into tissues of the body. Its presence is readily detected by delicate electron-counter apparatus.

A radioactive phosphorus isotope was made from sulfur and fed (as a phosphate) to an adult rat. In one week 29 per cent of the dose was found in the bones and some in the teeth and liver.

The Geiger-Müller counter is a vacuum tube with cathode and anode and a window through which electrons emitted from the nuclei of radioactive atoms may enter. These fast electrons create ions by stripping electrons from gas atoms in the tube. The increased conductivity of the gas causes a discharge in the tube, amplified by a suitable device to produce audible clicks in a loud speaker or other useful effects.

The Geiger counter is a warning watchdog for scientists working with an atomic energy pile. Lawrence held it close to the thyroid gland of a friend who drank a "cocktail" containing a compound of radioactive iodine a few hours earlier. They heard the clicks.

Radioactive iron (half-life of 10 years) appears in cows' milk within five minutes after feeding the animals a compound containing this iron.

Radio-chemical detection of elements is much more delicate than common chemical detection. By chemical means 10^{-7} grams of arsenic can be detected but as little as 10^{-17} grams of a radioactive isotope of arsenic can be detected by its beta radiation.

EVENTS IN NUCLEAR CHEMISTRY

1789	Uranium discovered by Klaproth
1896	Uranium radiations observed by Becquerel
1896	Radioactivity studied by the Curies
1898	Radium discovered by Madame Curie
1909	Radon change into helium observed by Rutherford
1919	First artificial disintegration of an element (nitrogen, oxygen) caused by Rutherford
1931	Neutron identified by Chadwick
1934	Neutrons from light elements by The Curie-Joliot
1935	Neutrons added to nucleus of uranium by Fermi
1939	Uranium fission with release of great energy due to neutron bombardment brought about by Hahn and Strassman; interpreted by Meitner and confirmed at five research centers
1940	Atomic bomb research begun in the United States
1940	Neptunium (${}_{93}\text{Np}^{239}$) made by MacMillan and Abelson
1940	Plutonium (${}_{94}\text{Pu}^{238}$) made by Seaborg, Wahl and Kennedy
1942	First sustaining chain reaction
1945 (July 16)	First atomic bomb exploded at Los Alamos
1945 (Aug. 6)	Second atomic bomb exploded at Hiroshima
1946	Elements 95, americium, and 96, curium, made and identified by Seaborg and associates

The *positron* is the positive mate of the negative electron, the same in mass but opposite in charge. Anderson in 1932 secured many photographs of fog tracks of positrons thrown out when cosmic rays disrupted certain atoms. Later, positrons were emitted when beryllium was bombarded by alpha particles.

Mesons, hitherto known only as resulting from cosmic rays, were produced in 1948 by cyclotron bombardment, at the University of California. Some negative and some positive, they have about 200 times the mass of the electron. They last a few millionths of a second and change into energy.

Exercises

1. What was the scientific foundation for the atomic bomb effort?
2. How will we get electric power out of uranium?
3. What are the chemical properties of plutonium?
4. How can C^{14} aid botanical research? Medical research?
5. How did we learn that the neutron had no charge?
6. Is there any hope that the meson can be put to work?

7. How was U^{235} separated from U^{238} ?
8. Where do we get the radioactive isotopes used in medical and botanical research?
9. What are the uses of the Geiger counter?
10. What do we mean by a "chain reaction"?

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Chapter 29 THE ATMOSPHERE. THE ARGON FAMILY

THE ATMOSPHERE

The atmosphere is worthy of study. Apparently so light that it scarcely impedes our movements, it presses upon us with a weight of nearly 14.7 pounds per square inch. The air resting on a single acre of earth weighs over 40,000 tons but at 3.6 miles the weight is only half as great.

High-Altitude Problems. Airplanes 4 miles up find the air pressure too low for operation of the motor. Consequently a supercharger is employed to feed air at proper pressure into the engine. Oxygen cylinders are needed by the pilot. Planes have risen above 10 miles.

Even at 15,000 feet the air pressure is only about one-half that at sea level and pilots put on an oxygen mask attached to a cylinder of compressed oxygen. The air-tight cabins of the new superbombers have normal air pressure maintained by pumps. At 29,000 feet temperature problems become serious, and electrically-heated clothing is required because the temperature falls to -44°C . (-47°F .). At 40,000 feet (-67°C .) natural rubber becomes almost as brittle as glass and ordinary lubricating oil stiffens like cold tar.

Military aviators carry, attached to a trouser leg, a small cylinder holding 38 quarts of compressed oxygen. If they "bail out" at a height of seven miles, this oxygen must last for the 10 minutes of descent before the parachutist reaches a livable density of air.

Air a Mixture. About 99 per cent of air is composed of two gases, oxygen and nitrogen, and the proportions of these vary but slightly. Several other substances are present, some in proportions that vary considerably. The approximate composition of dry air is given below.

Nitrogen	78.00 per cent (volume)
Oxygen	21.00
Argon	0.933
Carbon dioxide	0.03
	<hr/>
	99.963

In addition to the four substances named above there are found water vapor, helium, neon, krypton, xenon, dust, and sometimes ozone, hydrogen sulfide, and oxides of nitrogen in traces. Obviously the dust content varies with the wind and other factors, and water vapor may be present in excessive amounts in the jungle, or nearly lacking over the desert.

The evidence that these various constituents are present merely as a mixture and not as one compound is convincing:

1. Each constituent of the air retains its own properties irrespective of the presence of the others. The oxygen is just as soluble in water as if the nitrogen were missing.

2. The properties of air are the mean of the properties of its components, which is not true of a compound. The density, for example, is what might be calculated from such a mixture.

3. When liquid air evaporates, the more volatile nitrogen tends to escape faster than the oxygen. (In pure compounds, water for example, the distillate has exactly the same composition as the original liquid, unless decomposition occurs.) Therefore air can be separated into its constituents by liquefaction and fractional distillation. Compounds cannot.

4. Nitrogen and oxygen can be mixed in the same proportion as found in air, without change in temperature or volume, and yet produce a mixture like air. Evidently no reaction occurs.

5. The proportions by weight cannot be represented by a chemical formula because the constituent gases by weight are not found in exact multiples of atomic weights. This alone is a clinching argument.

Exercise

1. Why doesn't the oxygen, heavier than nitrogen, settle and the nitrogen rise?

The Oxygen-Carbon Dioxide Balance. It may seem alarming to learn that there are 2450 thousand million tons of carbon dioxide in the atmosphere, but this means only three parts in 10,000 of country air or twice that much in city air. We can live in air containing many times that amount of carbon dioxide.

This carbon dioxide has its source in the decay and fermentation of animal and plant bodies, in volcanic eruptions, in the respiration of animals, and in the combustion of fuel. Carbon dioxide even issues from the earth in some mineral springs. The world burns over 1,300,000,000 tons of coal annually, but even so this would have to be kept up 600 years to double the present amount of carbon dioxide — if none were removed from the air.

The average man inhales 17 cubic feet of air per hour and exhales 0.6 cubic feet of carbon dioxide, along with the unused nitrogen.

Humidity. Air can take up water vapor until the partial pressure of the water vapor equals the saturation value of the vapor tension of water at that particular temperature. The humidity is then 100 per cent and the air is saturated with moisture.

Air saturated at 20° has a vapor pressure of 17.4 mm. If the total pressure of the air is 750 mm., then $\frac{17.4}{750.0}$ or about 2.3 per cent of it is due to water vapor. In other words, about 2.33 per cent of the air under those conditions is water vapor. Of course each constituent gas occupies the entire volume.

2. What would be the weight of water in 650 cubic meters of air saturated at 25° C.? Remember the use of the G. M. V. and consult table on Vapor Tension in the Appendix.

On cooling this air to 10° the vapor pressure becomes only 9.18 mm. The difference between this and the amount held at 20° is precipitated as dew, fog, or rain.

If, however, air saturated at 10° is warmed to 20° , it is no longer saturated (that is, if it is not in actual contact with a body

of water). Its vapor pressure is still only 9.18 mm., while air at 20° is capable of holding nearly twice as much moisture. The humidity is not 100 per cent, but $\frac{9.18}{17.5}$, or 52.5 per cent.

A crystal will deliquesce in an atmosphere with a higher relative humidity than that present in a closed space about a saturated solution of that crystalline substance. Indicator crystals, small pinhead fragments, in air barely above such a limiting relative humidity will require an hour or two to show a wet margin when viewed under a low-power microscope but in air of relative humidity only a few per cent higher will deliquesce to give a pool in a few minutes.

In *Chemical Industry*, 58, 162 (1939) a reference table for such experiments is given in full:

RELATIVE HUMIDITY ABOVE SATURATED SOLUTIONS

Closed Space at 20°

Potassium Acetate.....	20%	Sodium Chloride.....	75%
Magnesium Chloride....	33%	Ammonium Chloride...	79.2%
Potassium Nitrate.....	45%	Potassium Bromide....	84%
Ammonium Nitrate.....	63%	Potassium Chromate...	88%
Sodium Nitrate.....	66%	Sodium Sulfate.....	93%

Nature's Balance. We might look into the future with the fear that robbing the atmosphere of oxygen and pouring carbon dioxide into it will finally make this globe uninhabitable. But fortunately nature maintains a beautiful balance. In utilizing the carbon dioxide plants keep the carbon and return the oxygen to the air.

But this is not the only safeguard. Carbon dioxide is soluble in water, so the quantity in the ocean is vastly greater than that in the atmosphere. Shell-fish take up immense amounts for their shells (calcium carbonate).

Dust. Very dirty air contains as much as 500,000,000 dust particles per cubic foot and even safe air carries 250,000 particles.

The dust falling on a square mile of Cleveland or a similar city in a year may total over 1000 tons. Unfortunately this dust is accompanied by a rain of sulfuric acid (many tons per square

mile) due to air oxidation of the sulfur dioxide from burning coal. The attack of this acid on buildings and trees is appalling.

"Laundered" air is required in many factories and electrostatic dust removers will probably become common in homes.

Air Conditioning. It is agreed now that the humidity of the air next the skin is an important factor in ventilation. The temperature of the human body is regulated to 98.6° F. by the evaporation of perspiration. Evaporation of 14 g. of water cools an average man more than 0.1° C. (or loss of half an ounce lowers the temperature about 0.2° F.). The evaporation of one quart removes 500 Calories. Nature regulates the evaporation to suit our needs. The layer of air in contact with the skin quickly becomes saturated and evaporation is checked unless fresh, dry air replaces this layer. Such replacement is effected by gentle air currents set up in our efforts to introduce outdoor air. Even a fan stirring the same old air produces greater comfort. The best practice today calls for blowing the fresh air through a spray of water to wash out dust and introduce enough (but not too much) moisture. In removing most of the dust the bacteria are also largely removed. The most comfortable humidity of air is from 50 to 60 per cent. However, in winter it is almost impossible to maintain this condition in our houses.

Air conditioning now means bringing the air of train, theater, home, or elsewhere to the temperature and relative humidity found most stimulating. During a hot and humid day the air-conditioning apparatus for a room $36 \times 42 \times 15$ feet will condense 27.5 gallons of water in 12 hours.

The deepest gold mine in the world, 8380 feet, in South Africa, reached its limit because of the air temperature, 100° – 120° F., and relative humidity, 95 per cent. A tremendous air-conditioning plant has been built to make further operation possible, for the ore is very rich.

Liquid Air. The liquefaction of air is an industry of considerable importance because it is the first step in securing oxygen and nitrogen for other industries. To liquefy the air it is first freed from carbon dioxide by washing with water and passing over lime. The air is then subjected to high pressure, and the heat of

compressing it to 200 atmospheres is removed by cooling with running water. Under such high pressure and slightly lowered

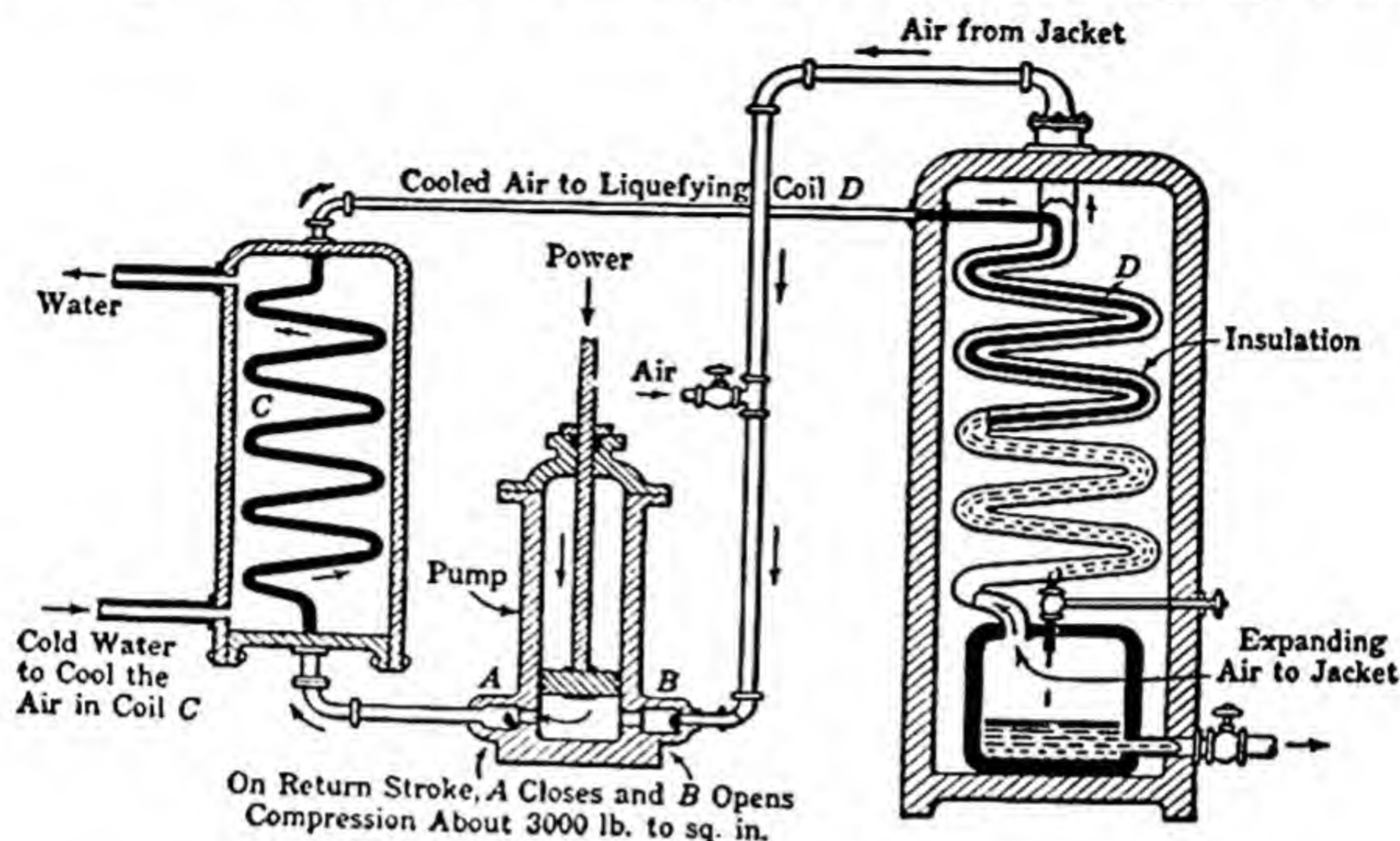


Fig. 111. Air-liquefying apparatus.

temperature the moisture in the gas is condensed. The last traces of water and carbon dioxide are absorbed by sodium hydroxide. The liquefier proper (Fig. 111) is nothing but a coil of very small copper tube with a valve to control the flow of air. The coil is contained in a metal jacket which is heat-insulated with wool. On opening the valve the compressed air expands as it escapes. This cools it somewhat. It is then made to travel back through the jacket, thus further cooling the air in the copper tube. After a few minutes this progressive cooling produces a steady stream of liquid air.



Fig. 112. Dewar bulb, the first thermos bottle.

The earlier Linde air-liquefaction machine used pressures as high as 200 times that of the atmosphere. Kapitza, the Russian physicist, secured greater cooling by allowing the expanding gas to drive a turbine (doing work removes heat faster) and is able to operate at an initial pressure of five atmospheres.

To keep the air liquid, use is made of a device invented by Dewar (Fig. 112). He made a double-walled flask and evacuated the space between the two walls, because a vacuum is a very poor conductor of heat. The inside walls were silvered also to reflect radiant heat. A cork stopper, loosely fitting, aided in heat insulation. Dewar, in 1892, found such flasks kept liquid air a surprising length of time. We use similar containers, to keep liquids hot or cold, under such names as "Thermos" bottles.

Read the splendid chapter on liquefaction of gases in the *Encyclopaedia Britannica*.

3. Why remove carbon dioxide and water vapor before liquefying air?

THE ARGON FAMILY

Argon. The fulfillment of prophecy is not confined to the Scriptures. Chemistry offers many examples. Back in 1785 Cavendish passed electric sparks through air, making the oxygen and nitrogen unite to form oxides of nitrogen, which he removed by reaction with a base. Excess oxygen was added to provide enough for all the nitrogen. Yet after removal of all the gases Cavendish could think of there was a little gas left, nearly one per cent of the original volume. His partial discovery lay unused for over a century, yet it was really a sort of prediction that a new gas would some day be found in the air.

In 1895 the English physicist, Lord Rayleigh, observed that apparently pure nitrogen made by removing everything else from air (as by Cavendish's method) was distinctly heavier than the unquestionably pure nitrogen made by decomposing ammonium nitrite. In fact he observed that one liter of nitrogen as prepared from air weighed 1.2572 g. while a liter of nitrogen from ammonium nitrite weighed 1.2506 g. Calling in the chemist, Sir William Ramsay, to help, Rayleigh proceeded to pass the "atmospheric" nitrogen over hot magnesium, which unites with nitrogen. They found a gas left over, evidently the same residue that puzzled Cavendish, for its volume was nearly one per cent of the original volume of air. Because it was chemically inert, they named the new element with the Greek word for "lazy," *argon*.

Ramsay used liquid air as a source of argon and found the last portions on evaporation rich in argon. This gas makes up 0.933 per cent of the air by volume. Millions of tungsten lamps are now filled with argon because by the use of this gas greater brilliance and longer life can be secured.

Read Rayleigh's own story of "Argon" in the *Encyclopaedia Britannica*.

Helium. The American chemist Hillebrand made the chance observation in 1889 that the uranium mineral, *uraninite*, on treatment with acids released a rather inactive gas (which he supposed was nitrogen). Years later Ramsay, in search of new sources of two rare gases, repeated Hillebrand's experiment, using the mineral *cleveite*, and secured a very inert gas different from any element then known. He found its spectrum identical with that of an element observed in the sun by Lockyer and Janssen during the solar eclipse of 1868. Soon afterward Ramsay isolated helium from the more volatile fractions of liquid air. Helium is so inactive that it has no compounds.

Caisson disease or "the bends" occurs when a worker comes too rapidly from high pressure to ordinary atmospheric pressure. Gas bubbles of escaping nitrogen affect the capillaries and the blood vessels of the brain. Since helium is less soluble in the blood it is safer to reduce pressure in steps with an atmosphere of helium and oxygen.

The United States is fortunate in owning the most workable sources of helium. The Petrolia natural gas of Texas contains 1 per cent helium. A well in New Mexico yielded natural gas containing 7 per cent.

In 1943 United States helium plants reached a capacity of 500,000,000 cubic feet per year. A modern airship could require 6,500,000 cubic feet for a filling and there is a constant loss by diffusion.

Large quantities of helium are used in dirigible balloons or blimps; to provide an inert atmosphere while welding magnesium; for decompression as divers return to the surface; and for some medical purposes. An atmosphere of oxygen and helium (instead of the heavier nitrogen) is easier to breathe than air.

(About 5 per cent of carbon dioxide stimulates breathing during resuscitation from shock or drowning.) An isotope of helium of mass 3 was concentrated from ordinary helium in 1948.

Neon, Krypton, and Xenon. After the discovery of argon and helium it was apparent that there must be three or four unknown elements in the same family in order to round out the Periodic Table. With this fact as incentive Ramsay carefully fractionated liquid air and obtained neon (Ne), krypton (Kr), and xenon (Xe). These "rare gases" — and they are truly rare, since only traces are found in the atmosphere — are quite inactive, like argon and helium. Neon conducts electricity seventy-five times as well as air.



Fig. 113. A simple vacuum discharge tube.

The Air-Separation Industry. To secure one pound of neon 44 tons of liquid air are required; 725 tons of air yield one pound of helium, 173 tons yield one pound of krypton, and 1208 tons yield one pound of xenon.

COMPOSITION OF ATMOSPHERE

	By volume
Nitrogen	78.03%
Oxygen	20.99%
Argon	0.94%
Hydrogen	1 part in 10,000 (?)
Neon	1 part in 65,000
Helium	1 part in 200,000
Krypton	1 part in 1,000,000
Xenon	1 part in 11,000,000

Substitution of argon, 1,000,000 cubic feet yearly, for the formerly-used nitrogen of our electric lamps saves us \$125,000,000 annually, yet if krypton and xenon from the air were substituted in these lamps a further saving of \$200,000,000 would be made. Argon lamps actually contain 86 per cent argon and 14 per cent nitrogen at a total pressure of one-third of an atmosphere.

The red luminous sign tubes are filled with neon (at low pressure), the blue with argon and mercury. This blue light in an amber tube produces green. Transformers raise the voltage for such lamps from 110 to 2000 or higher.

Ordinary neon is a mixture of isotopes (of masses 20 and 22) averaging 20.2 in weight since the lighter isotope is present in the larger amount (9 : 1).

"Heavy neon," 99 per cent pure, has been separated from its lighter isotope by utilizing the difference in rates of diffusion through porous solids.

Exercises

4. Why don't we gradually use up all the oxygen of the air and replace it with carbon dioxide?
5. Why is helium a valuable material resource? How do we know it is found in the sun?
6. If you passed steam and air over hot carbon, could you manage to get a mixture of nitrogen and hydrogen in the right proportion for ammonia synthesis?
7. With a relative humidity of 77 per cent at 20° how many kilograms of water vapor are contained in a room $40 \times 32 \times 20$ feet?
8. Why not fill our tungsten electric light bulbs with krypton since it is more efficient than argon for this purpose?
9. Why must water vapor and carbon dioxide be removed in an early stage of the separation of helium from natural gas?
10. What are the possible methods of removing excessive moisture from air in the process of "air conditioning"?
11. If the atmosphere were suddenly liquefied, how deep a layer would cover the earth? Atmospheric pressure is about 15 pounds per square inch and the density of liquid air is 0.92 g./ml. Find the metric conversion table in Appendix.

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Chapter 30 NITROGEN AND AMMONIA

NITROGEN

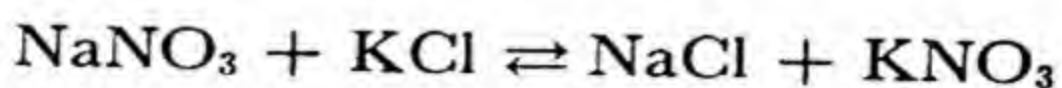
History of Nitrogen. Because of its comparative inertness, nitrogen was one of the least interesting of elements in the free state until a generation ago. Now it is eagerly sought after by basic industries of war and peace. Rutherford, the Edinburgh botanist, discovered the element in 1772, but it was not really considered an element until Lavoisier studied it.

Occurrence. Nitrogen is "as free as air," since it makes up four-fifths of the atmosphere. Pure nitrogen flows from a well drilled in Wyoming, probably as a residue from the reaction of air oxygen with materials deep in the earth. The nitrogen resting on every square foot of ground weighs almost a ton, while that resting on a square mile weighs 20,000,000 tons, enough, if converted into all the combined forms desired, to meet the world's needs for 12 years.

A small amount is found in the air as ammonia and as oxides of nitrogen, but these are washed into the soil by rains.

Deposits of potassium nitrate (KNO_3), or "saltpeter," are found, but are not of much consequence although in 1928 a large deposit was discovered in central Australia. Sodium nitrate (NaNO_3), or Chile saltpeter, is one of the most important sources of nitrogen compounds. In the rainless district of northern Chile there is a strip two miles wide by two hundred long and five feet thick that is rich in sodium nitrate. A little of the potassium salt occurs there also. By mixing solutions of sodium nitrate and

potassium chloride, and manipulating the concentration and temperature, a supply of potassium nitrate more than adequate for the world's gunpowder needs is secured:



This enormous deposit of sodium nitrate is also used extensively in the manufacture of nitric acid and fertilizers, so it has great economic significance. Since the discovery of the deposit in 1809, over 55,000,000 tons have been mined. Sales are now depressed by the success of the Haber process of making synthetic ammonia.

Since plants and animals eventually decay, their nitrogenous material is all-important in enriching the soil.

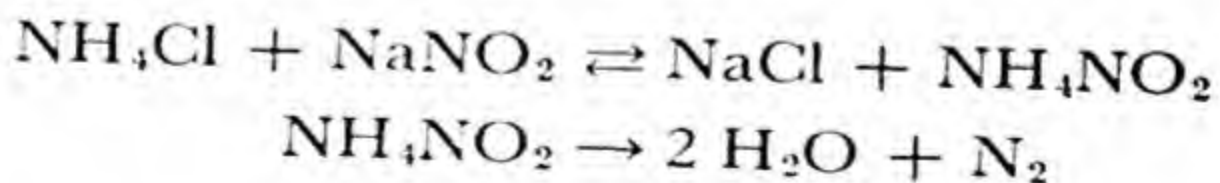
About 0.4 per cent of natural nitrogen is the heavy isotope, N^{15} .

Preparation. To prepare nitrogen it is a simple matter to pass dry air over hot copper, to remove the oxygen, forming copper oxide. If this oxide is reduced to the metal by a stream of hot hydrogen it is ready for use again. The remaining nitrogen is not quite pure, since it contains argon, carbon dioxide, etc.

The most important commercial source of nitrogen is now liquid air. When this modern product is allowed to evaporate, the more volatile nitrogen escapes first and is used chiefly in the manufacture of ammonia. It is fortunate for the cost of the process that there is a large demand for the oxygen as well.

Ammonium nitrite is an excellent laboratory source of pure nitrogen, although too expensive for commercial use. This salt is unstable, so it must be prepared when needed.

A solution of sodium nitrite is run steadily into a gently heated solution of ammonium chloride:



Since all four substances of the first equation are soluble, this is a reversible reaction, but when the mixture is heated the equilibrium is disturbed to the right since gentle heating decomposes the ammonium nitrite.

Exercise

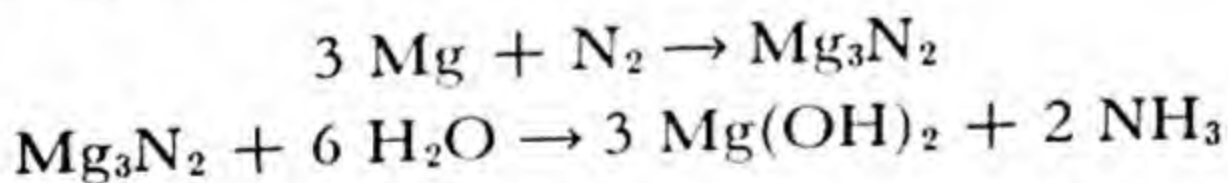
1. If 200 g. of copper oxide were reduced by hot ammonia gas, how many liters of nitrogen would be obtained? How many liters of ammonia would be required?

Physical Properties. Nitrogen is a colorless, odorless, tasteless gas, only slightly soluble in water. One liter weighs 1.2507 g., therefore nitrogen is a little lighter than air. At its critical temperature, -146° , it is liquefied by a critical pressure of 33 atmospheres. The liquid boils at -195.7° and freezes at -210.5° .

2. What two influences prevent all of the heavier oxygen of the air from settling to the surface of the earth, while the lighter nitrogen rises to great heights? There really is a certain amount of gravity separation. Why doesn't the heavy ozone of great heights settle to the ground?

"Ice" of frozen nitrogen glows with a brilliant greenish-yellow light under bombardment by cathode rays.

Chemical Properties. Nitrogen is found free in the atmosphere because it is so inactive. However, it combines with oxygen at the very high temperature of the electric arc or spark and with several other elements when strongly heated. With magnesium, aluminum, calcium, silicon, titanium, lithium, boron, and some other elements it forms nitrides of some interest as possible sources of ammonia by addition of water:

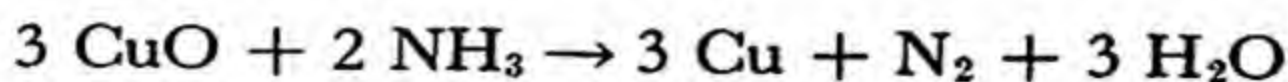


Hot calcium carbide unites with nitrogen to form calcium cyanamide, CaCN_2 . The union of nitrogen with hydrogen under the stimulus of a catalyst will be discussed in the ammonia section. (Haber Process.)

3. The G. M. V. of nitrogen weighs 28 g. What is the formula of the gas?

The composition of ammonia can be redetermined in the laboratory very easily by passing the gas (dried by soda-lime) over heated copper oxide (wire form preferred), collecting the water

formed in a weighed tube of soda-lime and collecting the free nitrogen over diluted acid:



The slight reactivity of nitrogen probably is due to the unusually high heat of dissociation of N_2 .

"Active nitrogen," prepared by a high-voltage discharge through ordinary nitrogen, combines readily with sulfur, unlike common N_2 . Doubtless the electric energy absorbed dissociates the molecule into atoms and forces some electrons farther out from the nucleus into higher energy levels.

Among the reactions of nitrogen (in some instances requiring the aid of catalysts, great pressure, or high temperatures) are

- (1) $\text{N}_2 + \text{O}_2 \rightarrow 2 \text{ NO}$
- (2) $\text{N}_2 + 3 \text{ H}_2 \rightarrow 2 \text{ NH}_3$
- (3) $\text{N}_2 + 3 \text{ Mg} \rightarrow \text{Mg}_3\text{N}_2$
- (4) $\text{N}_2 + \text{CaC}_2 \rightarrow \text{CaCN}_2 + \text{C}$
- (5) $\text{N}_2 + \text{Al}_2\text{O}_3 + 3 \text{ C} \rightarrow 3 \text{ CO} + 2 \text{ AlN}$
- (6) $\text{N}_2 + \text{Na}_2\text{CO}_3 + 4 \text{ C} \rightarrow 3 \text{ CO} + 2 \text{ NaCN}$

The interesting product of (4) is calcium cyanamide; of (6) is sodium cyanide.

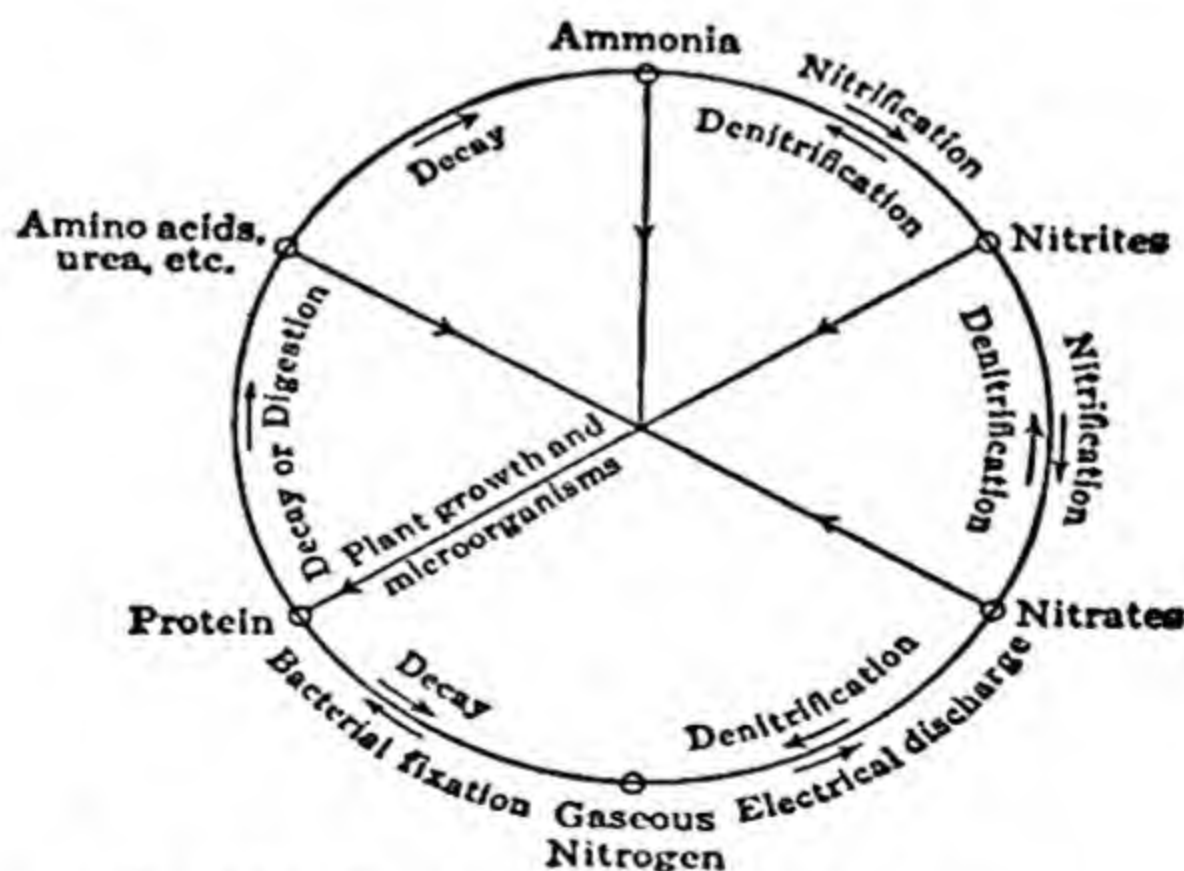


Fig. 114. The cycle of nitrogen in nature.

The Cycle of Nitrogen in Nature. Nitrogen is essential to plant life and hence to animal life (Fig. 114). Atmospheric nitro-

gen is seized by bacteria growing on the roots of clover, alfalfa, and the other legumes and converted into protein compounds and nitrates. When the clover is plowed under, its protein becomes a rich asset in the soil, subject to further improvement, of course, by the nitrifying bacteria. Succeeding crops of grain utilize the nitrates, animals eat the grain, and ultimately atmospheric nitrogen has become the protein of lean meat (muscle). Truly a wonderful magic! When plants or animals decay, some nitrogen is returned to the air and the cycle begins again.

AMMONIA

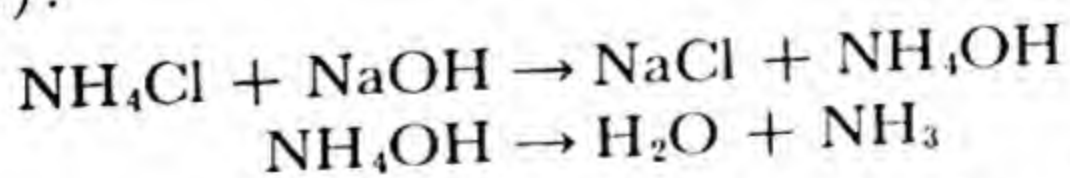
Ammonia has risen steadily in our esteem. Once of interest mainly as the pungent feature of a liniment, it later became important in the preparation of fertilizers, and during World War I rose to the rank of a military necessity. The fate of great nations hung upon their ability to produce more and more ammonia — from which they might make nitric acid for explosives. Now it dominates the future of agriculture as well.

Priestley (1774) was the first to prepare ammonia, collecting it over mercury. However, it was left to Berthollet to determine its true composition (1785). Faraday liquefied the gas in 1823.

Traces occur in the atmosphere, but there are no earth deposits of ammonia or its derivatives. On heating animal or plant substance containing combined nitrogen, ammonia always is formed. Manure piles liberate ammonia.

4. What was the original source of the nitrogen in coal?

Preparation in the Laboratory. The gas is conveniently prepared in the laboratory by warming a dry ammonium salt with lime or any other base. Since it is lighter than air, ammonia is collected by downward displacement of air (why not let it displace water?):

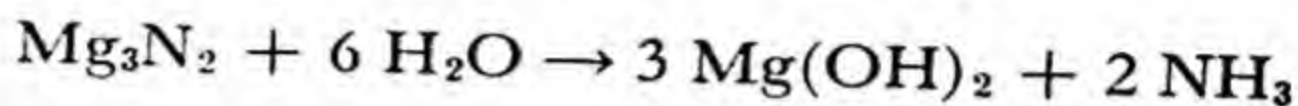


The ammonium hydroxide (NH_4OH) breaks down, when heated, into the gas and water. In fact warming a concentrated

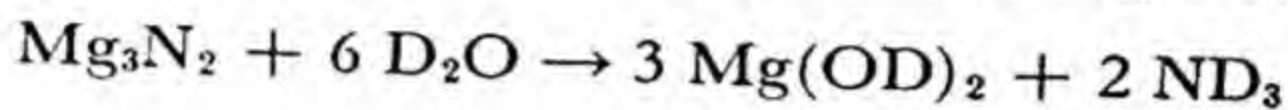
solution of ammonium hydroxide is often found a most convenient method of securing the gas. A so-called solution of NH_4OH actually contains much dissolved NH_3 .

For years Scotland has distilled her oil shales to get the oil. As a by-product enough ammonia is produced to form 42 pounds of ammonium sulfate per ton of shale. American oil-shale deposits are enormous.

Nitrides react with water to form ammonia:



With heavy water, heavy ammonia (ammonia- d_3) is formed:



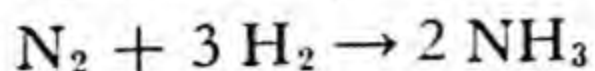
“Active” hydrogen reduces nitrites and nitrates to ammonia. If the hydrogen is prepared from zinc or aluminum and a base, the ammonia escapes; but if the hydrogen is prepared from zinc and an acid, the ammonia neutralizes the excess acid, forming a salt. How could you prove this?

Most protein material, when boiled with concentrated sulfuric acid, is decomposed with the formation of ammonia, or rather ammonium sulfate. This is the foundation of a famous method of food analysis. How could the amount of ammonia be determined?

Preparation from Coal. Soft coal contains one per cent, or a little more, of nitrogen. About one-fifth of this is recovered on distillation as ammonia. The mixed gas of distillation is passed through wash water which retains the ammonia and some impurities. Later, lime is added to this ammonia liquor and steam is passed through. The ammonia is thus driven off and may be neutralized with sulfuric acid to form ammonium sulfate (about 20 pounds from one ton of coal). In an average year the United States produces 900,000 tons of ammonium sulfate from coal (estimated as about 190,000 tons of “fixed nitrogen”).

Up to forty years ago coke was made in beehive coke ovens, allowing the ammonia and other gases to waste on the air. Now over 90 per cent of all American coke is made in by-product ovens with recovery of the ammonia, benzene, tars, coal gas, etc.

Synthetic Ammonia. By far the larger part of all commercial ammonia is prepared by the catalyzed high-pressure, high-temperature union of nitrogen and hydrogen:



This process (Haber) and its vital importance to the world are discussed under Nitrogen Fixation in the next chapter.

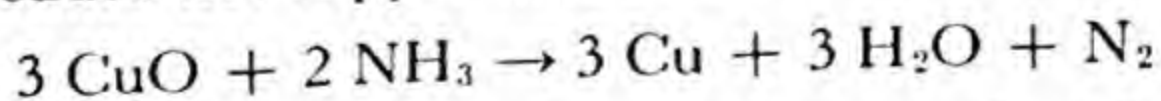
Physical Properties. Ammonia is a colorless, pungent gas about one-half as heavy as air. One liter weighs 0.7708 g. Its critical temperature is 133° and critical pressure 112 atmospheres. At 20° one volume of water absorbs 700 volumes of ammonia at 760 mm. pressure. The gas is also quite soluble in alcohol and in ether. At 10° it can be liquefied with a pressure of only 8.5 atmospheres. Its heat of evaporation is higher than that of any other known liquid except water. The concentrated solution in water has a density of 0.9 and contains about 28 per cent of the gas.

The very great solubility of ammonia in water may be shown by the experiment represented in Fig. 79. The flask is filled with dry ammonia and a few drops of water are then forced into the flask by air pressure (breath). The ammonia dissolves in these few drops, thus greatly decreasing the pressure of gas in the flask. Consequently water from the bottle is forced up the tube like a fountain. Could you do this with hydrogen chloride?

Chemical Properties. Long-continued breathing of air containing as little as one per cent of ammonia produces serious results. The gas may be burned in air by the use of a special device. In the presence of catalysts such as platinum ammonia reacts with oxygen to form oxides of nitrogen and water, hence nitric acid.

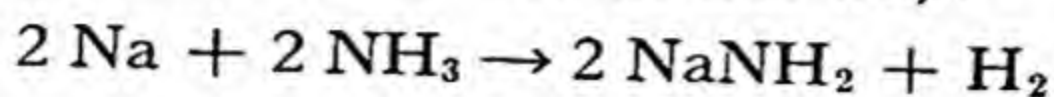
Ammonia burns with difficulty and yet in 1943 anhydrous liquid ammonia was used as a fuel for motor busses in Europe. Some ignition promotor had to be used.

Ammonia will steal oxygen even from metallic oxides. Its ability to reduce hot copper oxide has been mentioned:



Ammonia reacts directly with some hot metals to form nitrides such as Mg_3N_2 . It is actually used to harden the surface of steel by the formation of an iron nitride.

With sodium and potassium, ammonia reacts, when heated, to form amides. Sodamide is formed in this way:



Sodamide is much used in one of the syntheses of indigo.

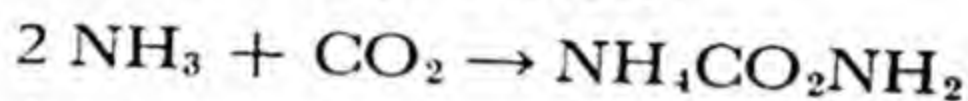
Acids react with the gas to form ammonium salts, but only in the presence of at least a trace of water:



One of the most important reactions of ammonia is with water to form ammonium hydroxide:

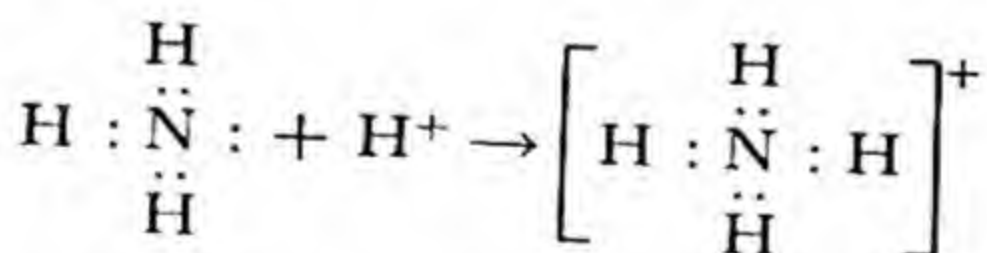
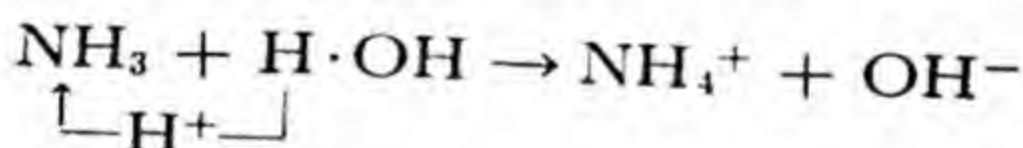


One might expect the reaction between ammonia and carbon dioxide to yield only ammonium carbonate, but as a matter of fact ordinary solid ammonium carbonate is really a mixture with ammonium carbamate, $\text{NH}_4\text{CO}_2\text{NH}_2$:



When this salt is heated it decomposes into urea, $\text{CO}(\text{NH}_2)_2$, and water.

In terms of the modern theory the NH_3 molecule may be said to accept a proton from a water molecule:

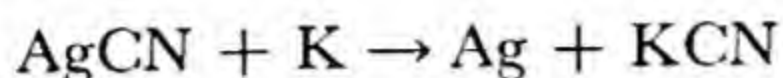


Ammonia reacts with some salts. With calcium chloride it forms $\text{CaCl}_2 \cdot 8 \text{NH}_3$, hence the gas must be dried over solid sodium hydroxide or some other dry base.

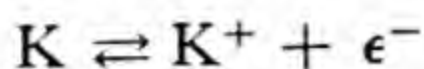
5. Why not dry ammonia by bubbling through concentrated sulfuric acid?

Liquefied ammonia as a solvent for acids, bases and salts, resembles water in many respects. Many organic reactions may be carried out in this solvent. The sodium and calcium groups of metals dissolve in it, with striking colors. Under such conditions

sodium and potassium can reduce silver chloride and cyanide to metallic silver.

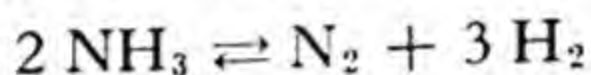


The good electrical conductivity of such solutions indicates that the metal is dissociated into metal ions and electrons.



In concentrated solutions the electrons are relatively free but on dilution electrons become associated with solvent molecules.

Ammonia can be cracked into its elements by heating in contact with the very catalysts used in its synthesis, proving that both reactions can be in equilibrium:



The cracking is 99.8 per cent complete at 500°. Cylinders of compressed ammonia are sold for such cracking when hydrogen is needed on a small commercial scale and when the accompanying nitrogen would do no harm.

Uses. Ammonia is the raw material for the Ostwald process of making nitric acid. It is combined with acids to make ammonium salts used in enormous quantities for fertilizers. Its salts are used in soldering, galvanizing, in dry batteries; and the gas itself is the chief refrigerant in commercial use.

In the modern ice plant ammonia liquefied under pressure and cooled by city water is allowed to expand through a coil of metal pipe (Fig. 115). The evaporation of the liquid ammonia and expansion of the gas reduce the temperature of a brine, surrounding the coils, below the freezing point of pure water. A concentrated solution of calcium chloride is the usual brine, because it freezes several degrees lower than pure water. Cans of water are immersed in the brine and their contents frozen to ice. It is a simple matter to lift out the cans and empty them. In cold-storage houses the rooms are chilled by pipes containing the circulating brine, and no ice need be made.

Household refrigerators which compress gases by electric power use either sulfur dioxide or Freon (CCl_2F_2) but refrigerators to be used on submarines must use Freon.

"When water is boiled by means of the heat from a flame, it is generally thought of as a heating process from the standpoint of water. It may be regarded, however, as a cooling process with respect to the fire. The hot products of combustion, passing around the vessel of boiling water, are cooled. If another liquid boiling at a lower temperature is used in the vessel, a fire may not be necessary to cause boiling, as the heat in surrounding objects may be sufficient to cause the boiling. This is especially true if the boiling point is very low, as

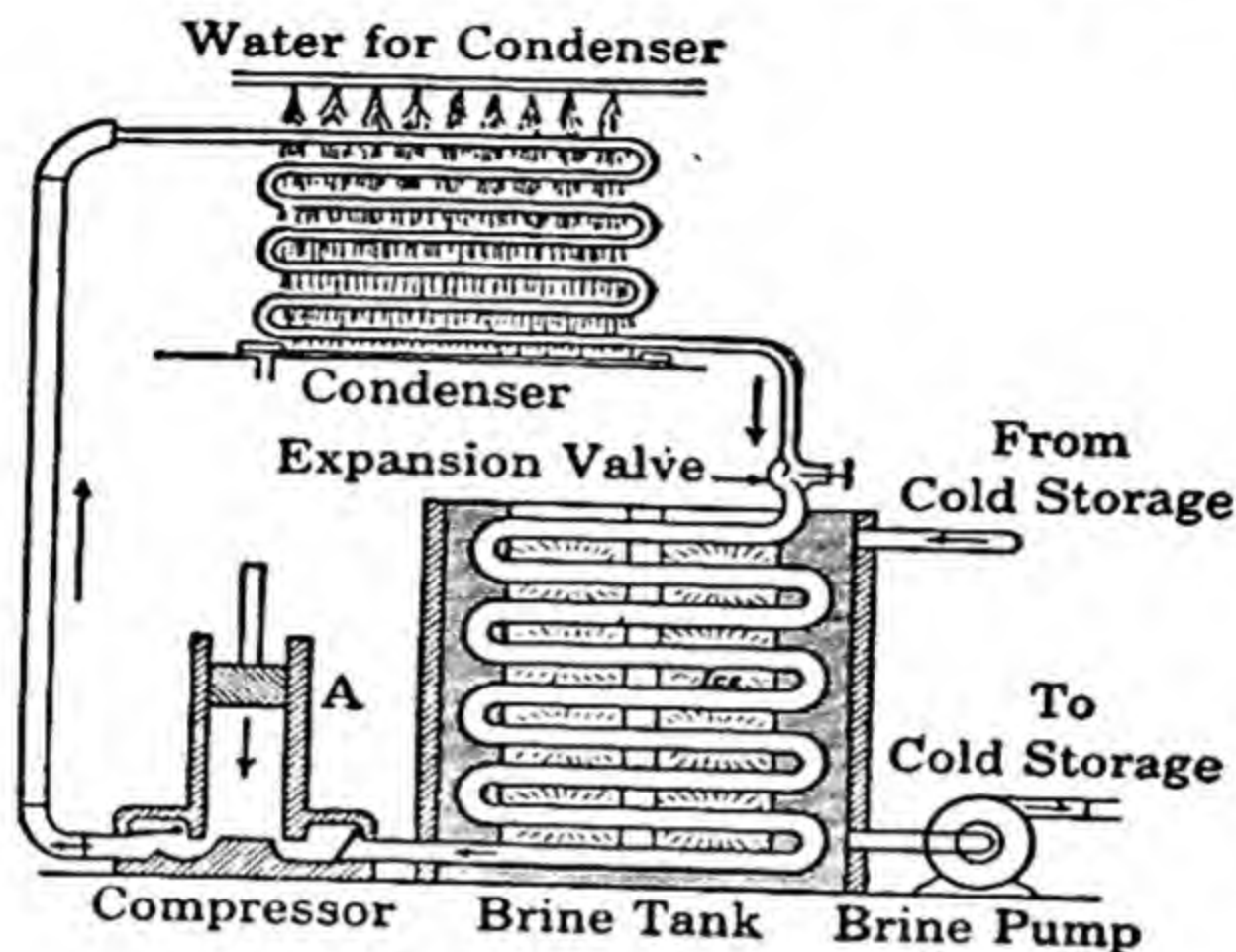
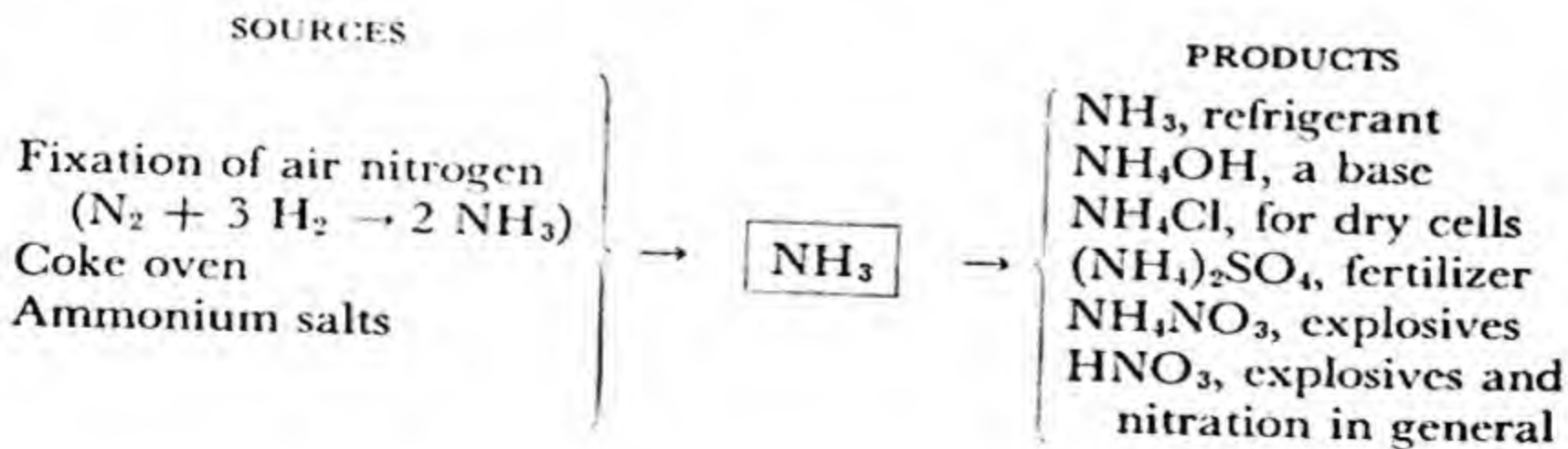


Fig. 115. Refrigeration with NH_3 .

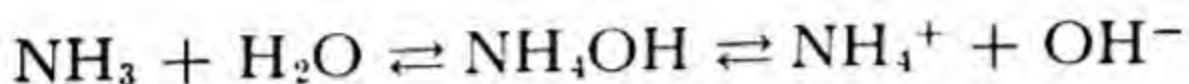
with anhydrous ammonia which has a boiling point of -28°F . If this liquid is placed in an open dish, it will absorb heat from surrounding objects and the atmosphere and boil violently. The outside of the vessel will become heavily frosted by moisture condensed from the air as a result of the low temperature of the vessel walls."—F. L. Kallam, *Chem. Met. Eng.*, 41, 192 (1934).

At 20°C . the pressure required to liquefy sulfur dioxide is 46 pounds per square inch; to liquefy ammonia, 120 pounds; and to liquefy carbon dioxide, 830 pounds.



6. The heat of fusion of water is 79 calories, while the heat of evaporation of ammonia is 258 calories. How many grams of liquid ammonia must be allowed to expand to a gas in order to freeze 8 kg. of water?

Ammonium Hydroxide. Ammonia not only dissolves freely in water, but to some extent reacts with water forming the very weak base, ammonium hydroxide. The equilibrium reactions are given:



Ammonium hydroxide is so unstable that its solutions contain much dissolved NH_3 .

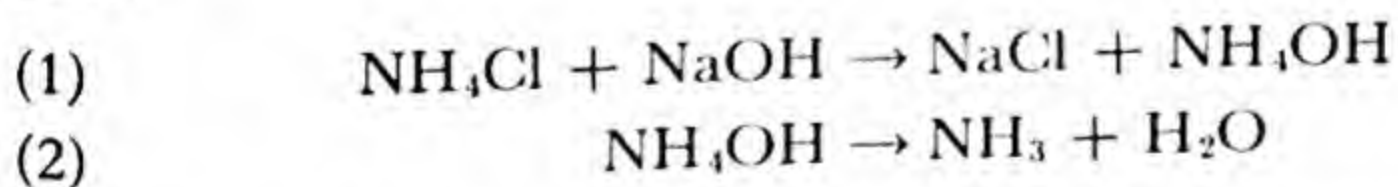
Ammonium Salts. *Ammonium sulfate*, formed by addition of ammonia water to sulfuric acid, is the salt usually used as a fertilizer. The United States made 900,000 tons in a recent year.

Ammonium chloride is useful in soldering and galvanizing. It dissociates, when heated, into ammonia and hydrogen chloride, which reunite, when cool, with the appearance of a smoke — solid particles of ammonium chloride.

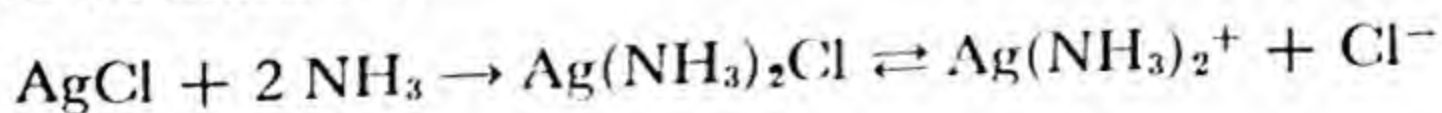
Ammonium nitrate has been used in enormous quantities in modern warfare as an explosive or in explosive mixtures. In a normal year this country makes 500,000,000 pounds.

When mixed with dynamite, ammonium nitrate can explode with tremendous force, yielding nitrogen, oxygen, and water vapor greatly expanded by the high temperature obtained.

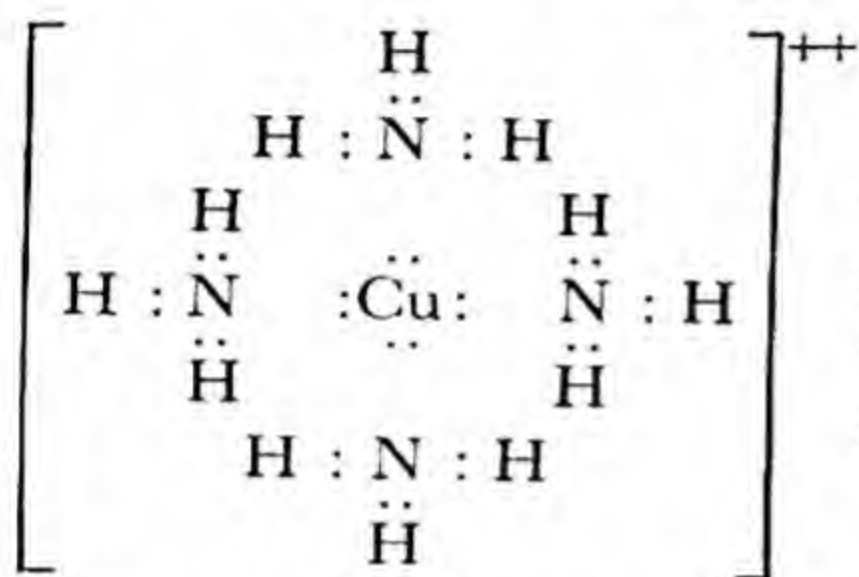
All ammonium salts decompose on heating, but they do not all release ammonia. However, any ammonium salt heated with a base releases ammonia, which can be recognized by smell or by its effect on wet red litmus paper. It is the only common volatile base:



Complex Ammonia Compounds. Many insoluble silver compounds dissolve in "ammonia water." Silver chloride may be used as an illustration:



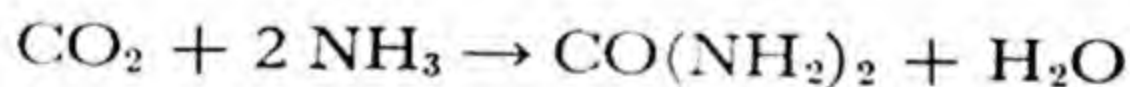
On ionization the ammonia goes with the silver and in electrolysis is released at the cathode. Adding ammonium hydroxide to a copper salt solution first precipitates copper hydroxide or, rather, a basic copper salt. An excess of ammonium hydroxide dissolves this, yielding a beautiful azure-blue solution. With copper sulfate the product is $\text{Cu}(\text{NH}_3)_4\text{SO}_4$ and with copper chloride $\text{Cu}(\text{NH}_3)_4\text{Cl}_2$. All these complex salts contain the $\text{Cu}(\text{NH}_3)_4^{++}$ ion. The formation of the peculiar blue color, quite different from the blue of Cu^{++} ion, is a test for copper compounds.



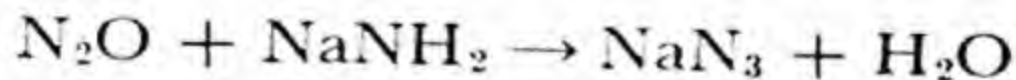
represents the azure-blue cupri-ammonia ion. The copper and all the nitrogen atoms have completed an octet outer layer of electrons.

Compounds Related to Ammonia. **Hydroxylamine**, NH_2OH , resembles ammonia in a number of properties. It is a strong reducing agent and forms salts with acids.

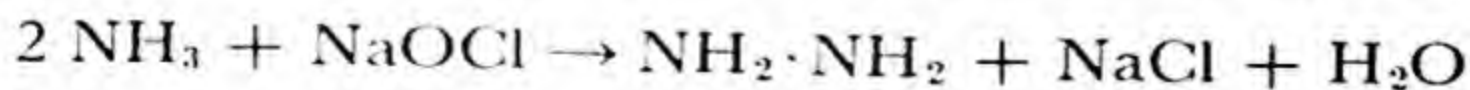
Urea, $\text{CO}(\text{NH}_2)_2$, useful in making one type of plastics and as a fertilizer, is easily prepared by reaction between carbon dioxide and ammonia



Hydrazoic acid, HN_3 , is a very explosive liquid compound as are its salts, the azides. Lead azide is used, like mercury fulminate, in detonating caps. At 190°



Hydrazine hydrate, $\text{NH}_2 \cdot \text{NH}_2$, a derivative of ammonia, was used by Germany in the propellant mixture of certain rockets.



Reaction between high strength hydrogen peroxide and calcium permanganate, releasing oxygen, furnished heat to generate

steam to drive a turbine which pumped hydrogen peroxide into a solution of hydrazine hydrate in methyl alcohol, the fuel.

It will be noted that both $\text{NH}_2 \cdot \text{NH}_2 \cdot \text{H}_2\text{O}$ and CH_3OH are oxidized by oxygen from the 85 per cent H_2O_2 .

Exercises

7. What weight of ammonium chloride must be used in the preparation of the ammonia necessary for 8 liters of 2.5 N ammonium hydroxide?
8. If 18 g. of magnesium nitride are treated with hot water, what weight of ammonia will be obtained? If this ammonia is made up to 500 ml., what will be the normality? How many ml. of 0.25 N hydrochloric acid will it take to neutralize 25 ml.?
9. Of what industrial importance are the rare gases?
10. If you were denied the use of a liquid-air apparatus but were permitted to burn hydrogen (supply guaranteed) in air, could you prepare a mixture of approximately three volumes of free hydrogen and one volume of free nitrogen for conversion to ammonia by the Haber process? Disregard the argon in air.
11. Priestley first made ammonia and recognized it as a substance but failed to determine its composition. How could you prove that it is a compound of nitrogen and hydrogen? How determine their proportions and therefore a simplified formula?

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Chapter 31 NITROGEN FIXATION AND PLANT FOOD

The real "conquest of the air" was not made by the inventors of airplanes and dirigible airships, but by the chemist. Before the end of the last century a world wheat famine was predicted by

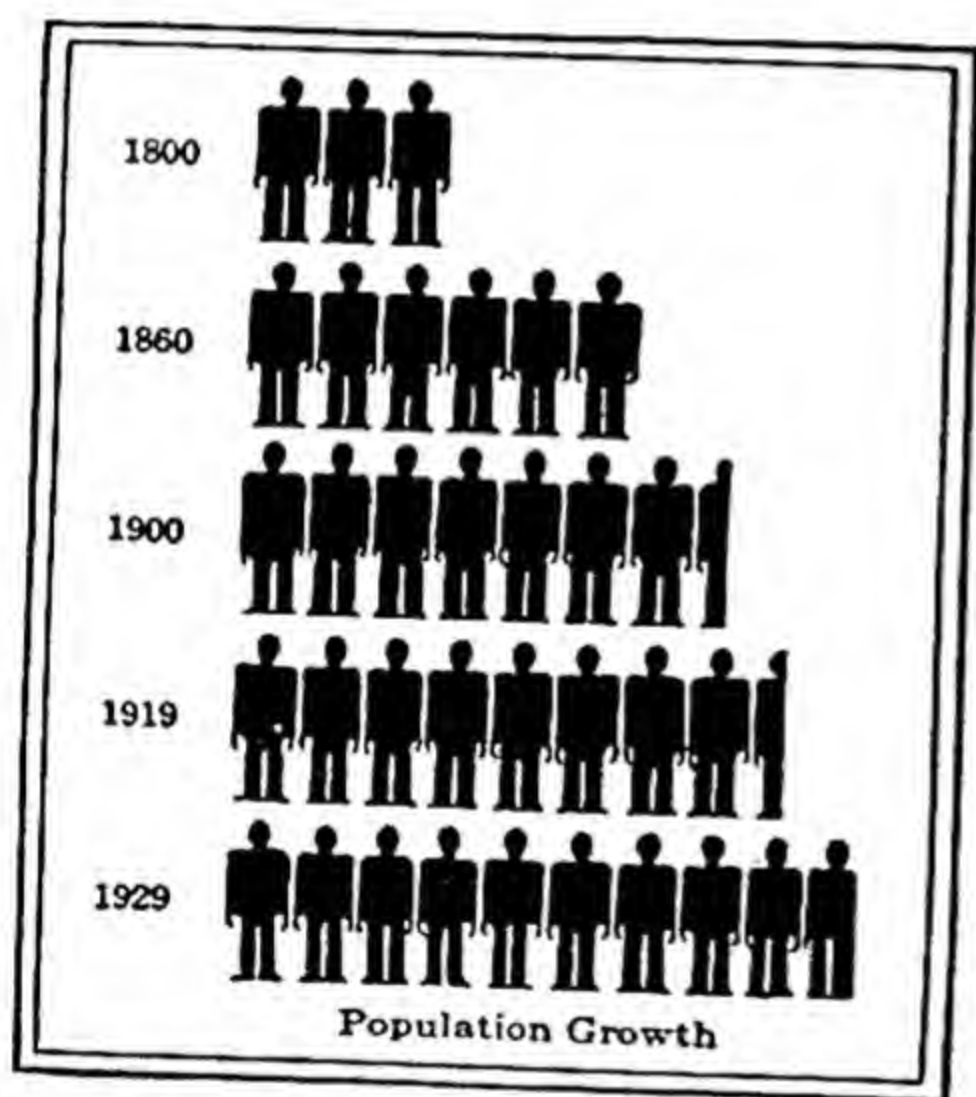


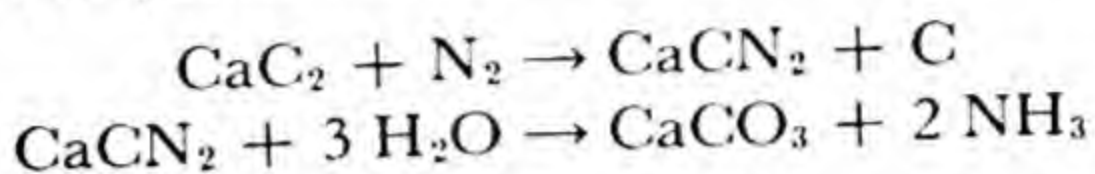
Fig. 116. Growth of world population, 1800 to 1929.

eminent scientists because of the probable early exhaustion of the sodium nitrate beds of Chile. The population of the world doubled between 1800 and 1900 and the rate of increase is still alarming. The chemist has driven off, for a long time to come, the specter of world starvation with its accompanying chaos, warfare, and human misery. His conquest of the air was the *fixa-tion of atmospheric nitrogen into compounds available as plant food or otherwise useful to man-kind*. He succeeded; not by a single method, but by three or four triumphs.

A nation lacking an adequate supply of combined nitrogen can be great neither in peace nor in war. Nitrogen compounds are essential to agriculture, to many basic industries, and to the manufacture of all useful explosives.

Fixation of Nitrogen by the Arc Process. The first chemical conquest of the air was by the arc process, now obsolete. It is discussed briefly on page 362.

The Cyanamide Process. In 1895 the German chemists, Caro and Frank, *reacted nitrogen from the air with calcium carbide in an electric furnace, forming calcium cyanamide* (CaCN_2), a useful fertilizer and a source of ammonia. It was not until 1906, however, that commercial plants were built (in Germany and Italy).

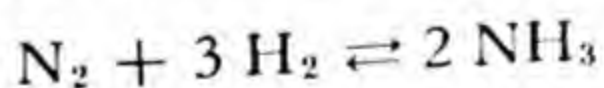


The cyanamide process of nitrogen fixation has lost, probably forever, its leading place. Curiously enough it reached its world-record production in 1936-37.

THE DIRECT SYNTHESIS OF AMMONIA

The Claude-Haber Process. The process of making ammonia by direct union of the elements was first made a commercial success by Haber in Germany (1913). This was, perhaps, the greatest triumph of chemical engineering, and Germany may well be proud of Haber. Without his process, she could not have continued World War I a year for lack of high explosives. Ammonia \rightarrow nitric acid \rightarrow explosives was the order of the day. Her other sources of ammonia, though great, were inadequate. Without control of the sea, the usual importation of sodium nitrate from Chile was impossible. So a scarcity of nitric acid would have been inevitable but for the brilliant Haber.

Haber developed the reaction between nitrogen and hydrogen:



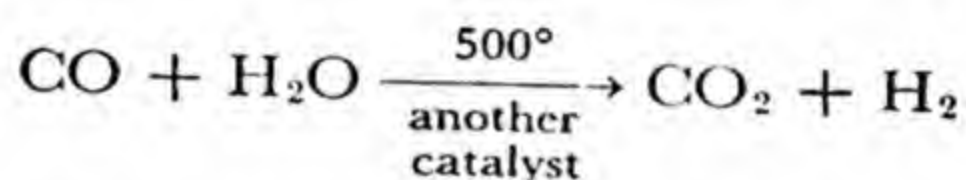
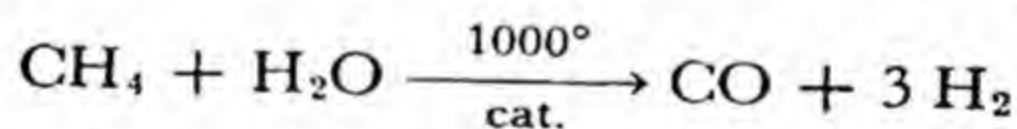
At ordinary temperatures their union to form ammonia is so slow as to be imperceptible, while at high temperatures the ammonia is decomposed rapidly. In fact above 700° it is almost completely decomposed. Obviously a moderate temperature is desirable, but even so, the yield is poor. Haber discovered that at 200 atmospheres pressure and 500° the formation of ammonia proceeds satisfactorily if osmium or uranium is present as a catalyst. Work-

ing at such high temperatures and pressures is difficult, yet success was obtained. Chrome steel free from carbon must be used for the apparatus, as otherwise the hydrogen removes the carbon from ordinary steel, leaving "rotten steel." The catalyst now used is essentially iron with some substances such as the oxides of aluminum and potassium to promote the catalytic action.

Claude, in France, improved the process by increasing the pressure to 1000 atmospheres or more.

Sources of Hydrogen for Direct Ammonia Synthesis. In some sections of Europe hydrogen is removed from coke-oven gas by a liquefaction process but the market value of this gas in America is too high to make this a suitable source. In Italy cheap electricity leads to some use of pure electrolytic hydrogen from water. The original German Haber process obtained its hydrogen from water gas (coke and steam) by methods outlined in the Hydrogen chapter and this seems to suit American costs best at present.

Recently natural gas (largely CH_4 , methane) with steam and air entering into the reactions has been used as a source of the hydrogen and nitrogen required for ammonia synthesis.



The necessity of removing from the nitrogen (liquid-air source) and hydrogen all such catalyst poisons as carbon monoxide, sulfur compounds, phosphine, and water, adds greatly to the cost.

World Production. Prior to World War II, nitrogen fixation plants were overbuilt and the world capacity of nearly 4,000,000 tons of fixed nitrogen was 50 per cent in excess of the normal consumption. At least a dozen countries, great and small, are now practically independent as far as ammonia, ammonium salts, nitric acid, and nitrates are concerned. Our own country can produce well beyond our needs in peaceful times. Furthermore, the prices of the products have fallen.

Our own production can equal 200,000 tons (as combined nitrogen) from coke ovens and 1,000,000 tons or more from synthetic processes.

Competition

Uses:

Processes to make:

Synthetic NH_3

Chilean nitrate

Cyanamide

Organic

(urea, tankage,
manures, etc.)

Soil bacteria

(on legumes)

NITROGEN

FERTILIZER

Indispensable for
plant growth

SOIL FERTILITY

Fixation of Nitrogen by Bacteria. Bacteria, those microscopic organisms of the fungus type which cause so many of our diseases, are wonderful little chemists. In the human body they make poisons that sometimes kill. In the soil some types "fix" the free nitrogen of the air into nitric acid, which, of course, reacts with the basic material always in the soil to form nitrates, choice plant food. The nitrifying types are not found in all soils, but they are always found in little lumps or nodules attached to the roots of clover, alfalfa, cowpeas, and other legumes. Clover thrives on a soil that contains enough of these friendly bacteria. Sometimes the farmer inoculates seeds very cheaply with the proper bacteria. One gram of rich soil may contain millions of bacteria. As a good air supply is necessary to stimulate nitrate formation, soil must not be allowed to become too compact or water-logged. Organic matter (humus) is also needed to supply food for bacteria.

Problem Yet to Be Solved: to learn how bacteria, without the high temperature of the arc process or the great pressure of the synthetic ammonia processes, are able to "fix" the free nitrogen of the air.

Plant Food. It is generally believed that only ten chemical elements are necessary as food materials — nitrogen, phosphorus, potassium, carbon, hydrogen, oxygen, sulfur, calcium,

iron, and magnesium — but recently it has been demonstrated that manganese, copper, zinc, and boron in traces, at least, are essential to the healthy growth of certain plants. Ten of these elements are supplied in most soils (supplemented by the atmosphere), but heavy cropping finally forces a fertilizing replacement of nitrogen, potassium, and phosphorus compounds. The best commercial fertilizers contain the essential trace elements.

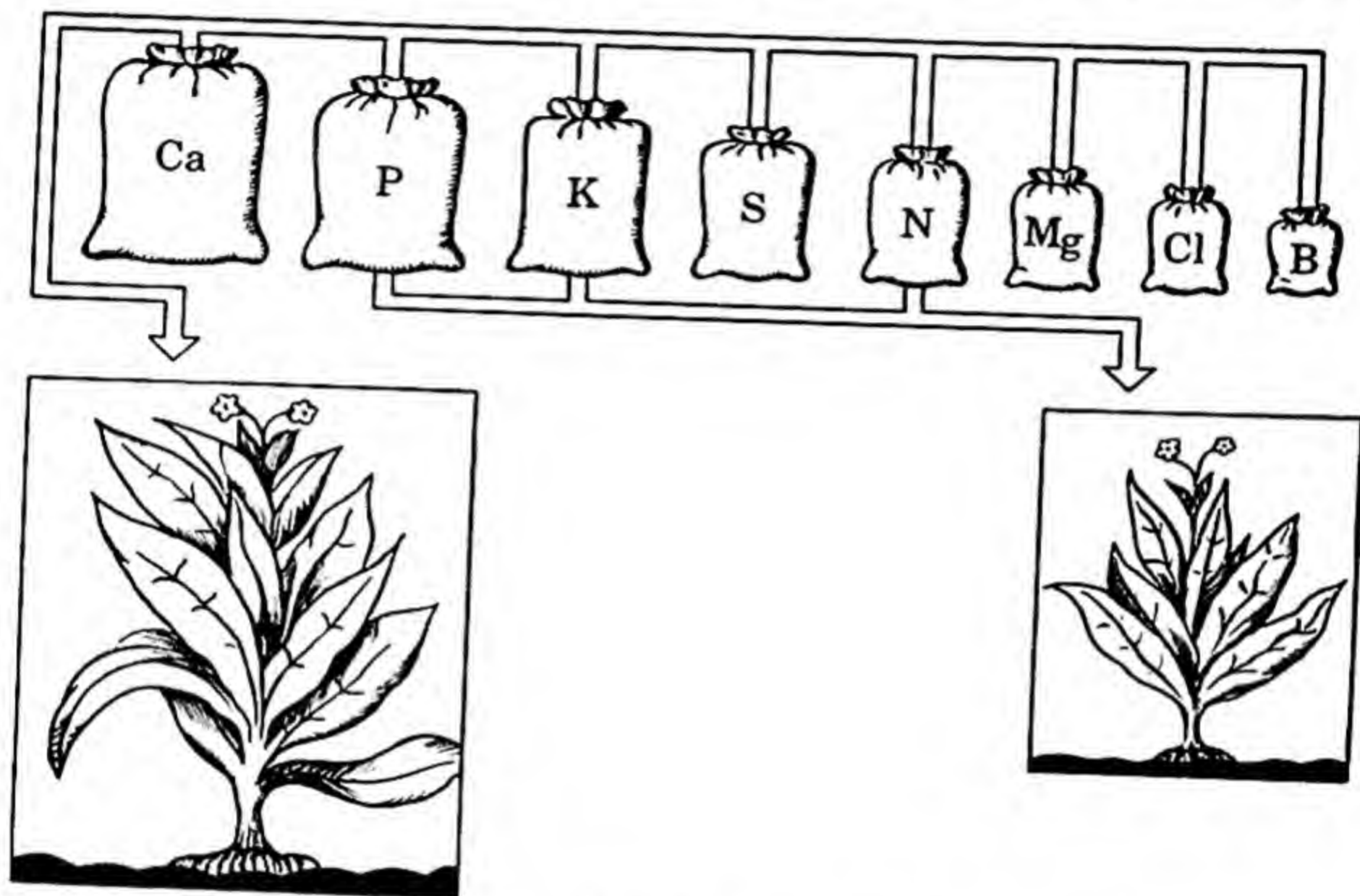


Fig. 117. The tobacco plant on the right was fed by a fertilizer limited to the traditional phosphate, potash, and nitrogen. A similar but much larger tobacco plant on the left was fed by a fertilizer containing eight elements essential to the best growth. (Courtesy *The Country Gentleman*, Philadelphia.)

Although ammonium salts are used as a source of nitrogen it has been shown that ammonia solutions are effective, and cheaper.

Decayed organic matter (from stable manures and plowed-under crops) called "humus" is essential, for it retains water, binds sandy soils and loosens clay soils, renders much insoluble plant food available, holds in combination large quantities of useful lime, and aids in the growth of beneficial bacteria. The physical and biological condition of soils is important.

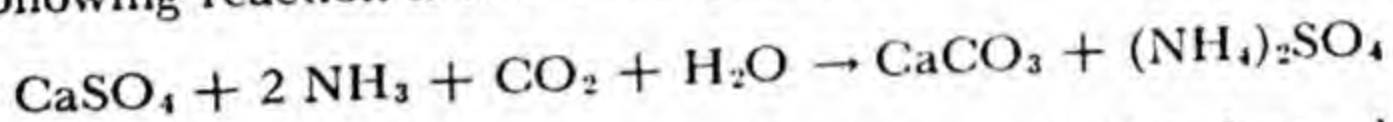
The sources of potassium salts and phosphates are discussed in other sections of the text. See Index.

Growth hormones for plants are receiving great research attention. Indole acetic acid, for example, greatly increases the tendency of cuttings to throw out roots.

Hydroponics, or soil-less farming, is a process of growing fresh vegetables in water solutions of plant food (tanks). The advantage for airplane depots on remote barren islands is obvious. The U. S. Army in Japan also has set up a large farm of these tanks in order to grow certain vegetables free from soil contamination.

Exercises

1. If overcrowding leads to war, how can the yeast plant work for peace?
2. What are the sources of hydrogen for Nitrogen Fixation?
3. The following reaction is said to be possible:



Why may this become important to Germany with her large deposits of gypsum, lack of sulfur, and deficiency in good iron pyrites?

4. From 980 g. of nitrogen how many grams of ammonia could be prepared by the Haber process? How many grams of nitric acid by the further step of the Ostwald process; catalytic oxidation?

References

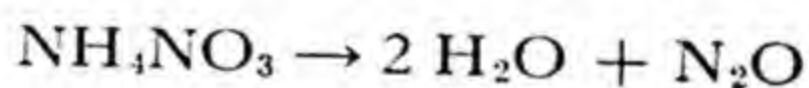
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Chapter 32 THE OXIDES OF NITROGEN. NITRIC ACID

A PARTIAL COMPARISON OF THE OXIDES OF NITROGEN

N ₂ O	Nitrous oxide	Colorless gas	Heating NH ₄ NO ₃
NO	Nitric oxide	Colorless gas	Diluted HNO ₃ on Cu
N ₂ O ₃	Nitrogen trioxide	Blue liquid at - 21°	Cooling NO + NO ₂ ⇌ N ₂ O ₃
NO ₂	Nitrogen dioxide	Red-brown gas	Conc. HNO ₃ on Cu
N ₂ O ₄	Nitrogen tetroxide	Pale yellow gas	Cooling 2 NO ₂ ⇌ N ₂ O ₄
N ₂ O ₅	Nitrogen pentoxide	White solid	Dehydrating HNO ₃ by P ₂ O ₅

Nitrous Oxide, N₂O. It was Priestley who in 1772 first prepared nitrous oxide gas by reduction of nitric oxide with moist iron filings. Since it was thought to be poisonous, Sir Humphry Davy was a rash young man when he breathed some of it to learn its properties. The hysteria occasionally produced by nitrous oxide earned for it the name "laughing gas." The gas is now made by the careful heating of ammonium nitrate. (At too high temperatures ammonium nitrate may explode with terrific violence.)



Exercise

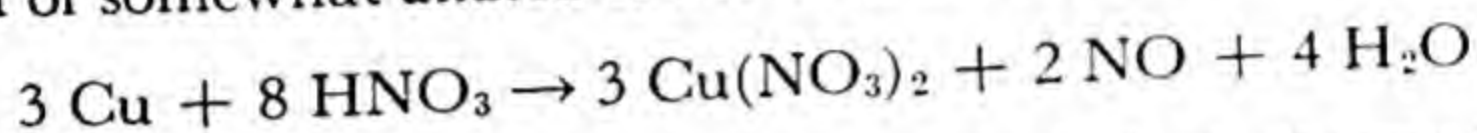
1. What ammonium salt is heated to prepare pure nitrogen?

Oxygen must be mixed with this gas when used as an anæsthetic. Formerly only dentists used this pleasant, quick-acting anæsthetic, but in recent years it has been widely used by surgeons.

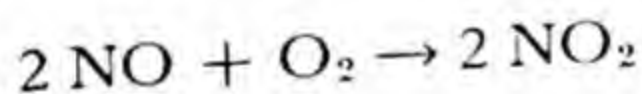
Since nitrous oxide is rather soluble, it is usually collected over warm water.

Nitric Oxide, NO. Although Cavendish in 1766 made this gas by passing electric sparks through a mixture of oxygen and nitrogen, and the lightning flash in air has been making it for ages, scientists had done almost nothing with this reaction before the present century. But early in this century nitric oxide became of such great importance that war and agriculture seemed likely to depend upon its formation by the arc process and its ready conversion into nitric acid.

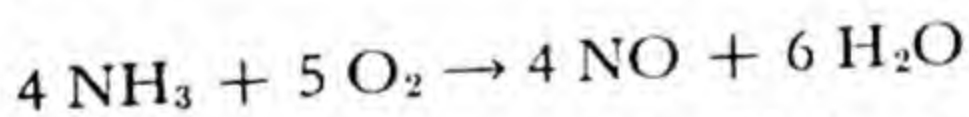
Nitric oxide is a colorless gas slightly soluble in water. The liquefied form boils at -153.6° . This gas is easily prepared by the action of somewhat *diluted* nitric acid on copper:



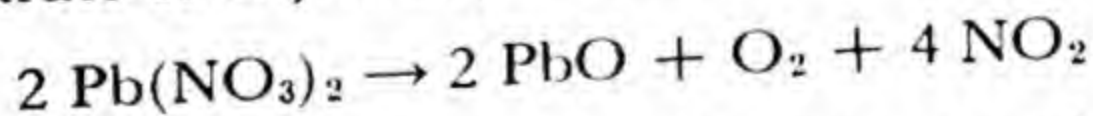
In making nitric oxide a red-brown gas is first observed, and after this product is swept out of the generating flask it is replaced by a colorless gas. The explanation is simple. Nitric oxide is colorless but reacts with oxygen of the air to form red-brown nitrogen dioxide:



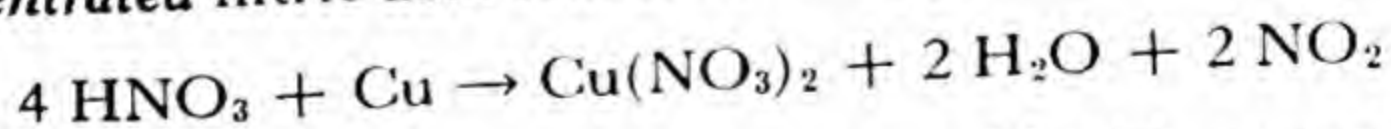
The first reaction in the catalytic oxidation of ammonia by air is:



Nitrogen Dioxide, NO₂ (Tetroxide, N₂O₄, cold). This very poisonous gas is made by heating pulverized lead nitrate or, in fact, the nitrate of any heavy metal:

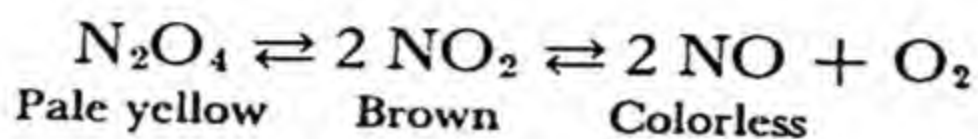


Concentrated nitric acid reacts with copper to release this gas:

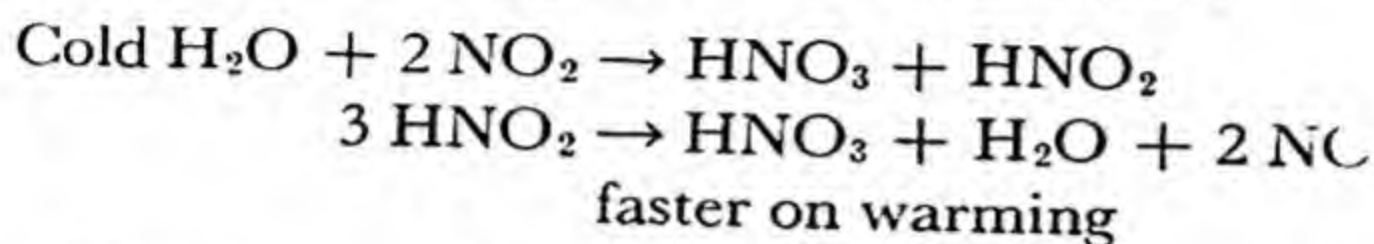


Above it was stated that *dilute* nitric acid with copper yields NO, nitric oxide. Below 22° the pale yellow nitrogen tetroxide (N₂O₄) exists. This dissociates completely into nitrogen dioxide (NO₂) at 156° . At intermediate temperatures mixtures of the two

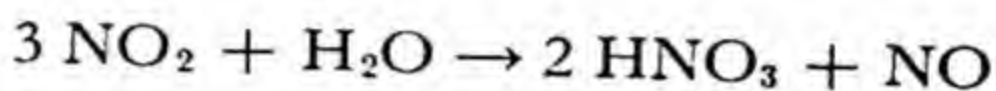
exist with corresponding densities. Above 620° all the NO_2 dissociates:



Its most interesting reaction is with water:



The reason there is no nitrous acid (HNO_2) formed in hot water is that it is decomposed by heat. The above equations may be condensed as:



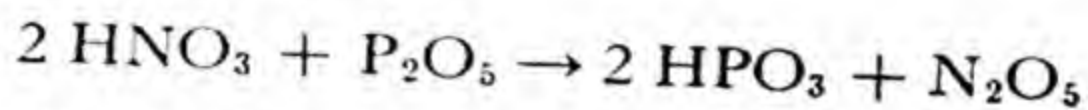
2. Could NO_2 be made at 700° ?
3. If a mixture of heated air and nitrogen dioxide were led through a tower down which a spray of water fell, what would become of the nitric oxide by-product?

Nitrogen Trioxide, N_2O_3 . This substance is formed by cooling a mixture of nitric oxide and nitrogen dioxide to -21° and appears then as a blue liquid. It dissociates well below room temperature, so as a gas it is really the brown mixture of $\text{NO} + \text{NO}_2$. The equilibrium proportions change with the temperature:



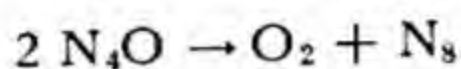
How does nitrogen trioxide function in the lead-chamber process of making sulfuric acid?

Nitrogen Pentoxide, N_2O_5 . This white solid is prepared by removing the elements of water from pure anhydrous nitric acid with phosphorus pentoxide. It is mainly a scientific curiosity, as the anhydride of nitric acid:



4. Nitrous oxide, when heated to high temperature, decomposes into nitrogen and oxygen. If 9 liters of nitrous oxide are decomposed by heat, what will be the volume of the resulting gas?

5. How many grams of ammonium nitrate would be required for the preparation of 17 liters of nitrous oxide measured at 21° and 12 atmospheres?
6. Twenty ml. of a 0.7 normal solution of nitric acid are treated with excess ferrous sulfate and sulfuric acid. What volume of nitric oxide is obtained?
7. A student once answered the question "How could you make oxygen from the air?" by this equation:



What is wrong? What led him to this answer?

8. Do you know of any great use of N_2O_3 as a catalyst?

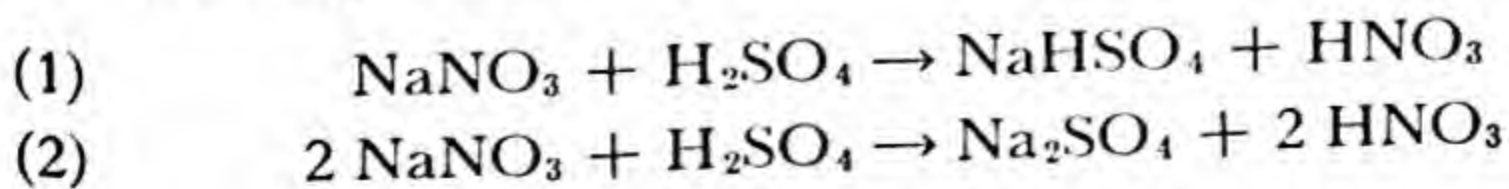
Nitrates in Nature. The largest deposit of nitrates is the sodium nitrate bed in the almost rainless Atacama Desert of northern Chile.

Potassium nitrate occurs to a limited extent in India (Bengal saltpeter) and is formed when organic matter decays in contact with wood ashes.

NITRIC ACID

This acid has played a great rôle in history (since the ninth century) and is even now at the front of the stage. Its salts are important fertilizers, supplementing ammonium sulfate and the other soluble nitrogen compounds. The acid is essential to the manufacture of most high explosives, of many dyes and medicines, of most movie film, and of numerous other useful products. In a recent year we used 800,000 tons.

Preparation from Sodium Nitrate. Basil Valentine in the fifteenth century simplified an earlier process by heating a mixture of sodium nitrate and "oil of vitriol" (concentrated sulfuric acid). The more volatile nitric acid escaped into a condenser. This ancient process still survives. In the laboratory a glass retort, with a cooled flask as condenser, is used (Fig. 118). Two reactions may occur, depending upon the relative excess of sodium nitrate and the temperature:



The first reaction is favored because it goes to practical completion below 200° C., while the second requires a temperature of 900° C. for completion.

Cast-iron stills are used commercially and the vapors are condensed in glass tubes or, more recently, in fused quartz or duriron

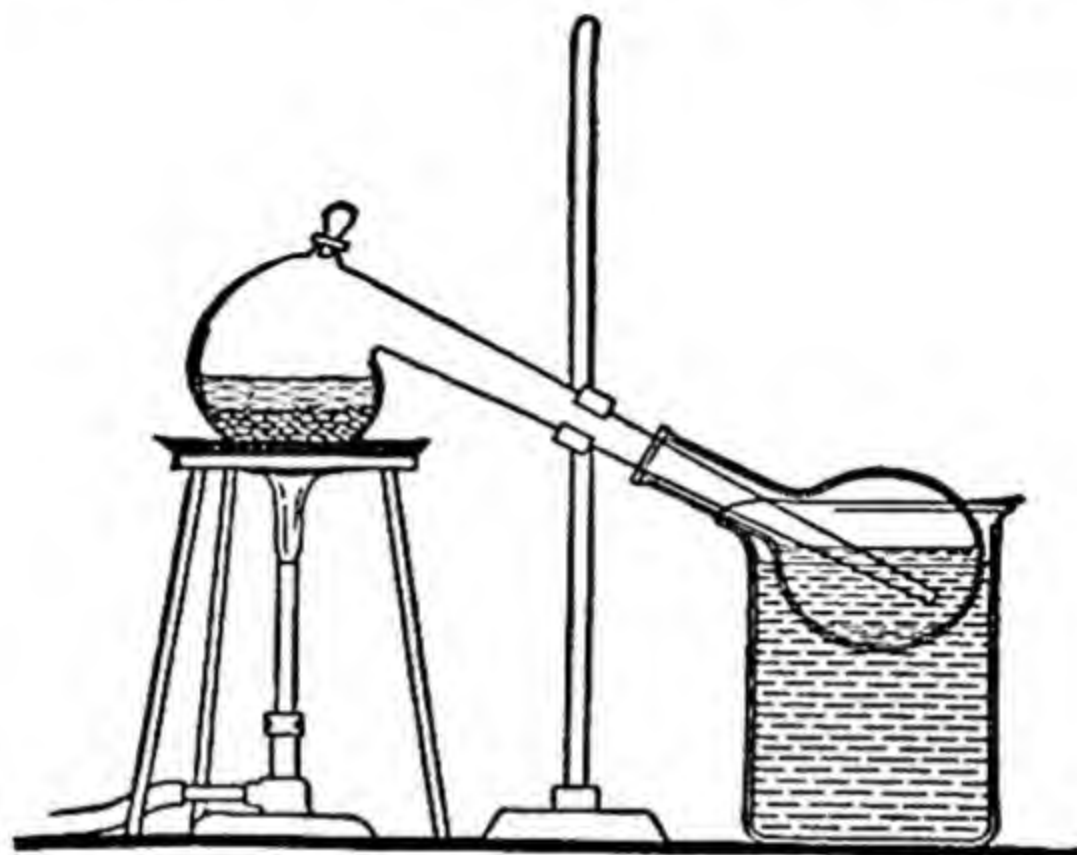
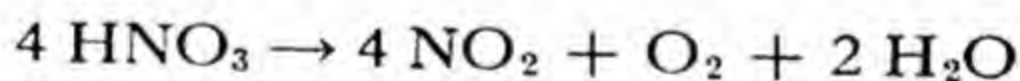


Fig. 118. Laboratory preparation of nitric acid.

tubes. Duriron, an iron alloy containing 16 per cent of silicon, resists corrosion by hot, concentrated nitric acid. Duriron is very hard to machine and is brittle.

On distilling nitric acid there is some decomposition as indicated below:



The ordinary "concentrated" acid of commerce is 68 per cent nitric acid and 32 per cent water.

The Arc Process. This process, now obsolete, utilized the high temperature of the electric arc to convert the oxygen and nitrogen of the air into nitric oxide and dioxide. With water the dioxide reacts to form nitric acid.

The principle of the old Birkeland-Eyde arc process has recently been applied successfully by Daniels and Hendrickson by means of their quick-cooling modifications. Air is blown through a hot bed of refractory pebbles to preheat it, then through an extremely hot gas-fired furnace and finally through

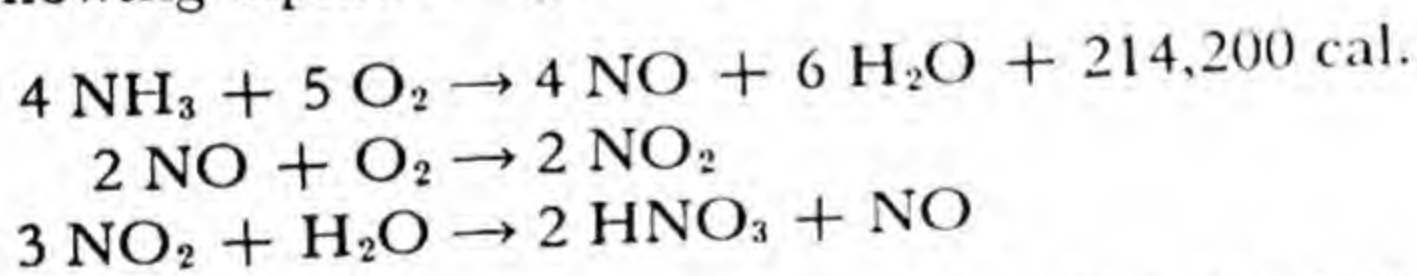
a second, cold pebble bed where the gas is chilled very rapidly to prevent thermal decomposition of the nitric dioxide. Pre-heating the air in a hot pebble bed makes possible the temperature of 2315°C . desired.

- (1) $\text{N}_2 + \text{O}_2 \rightarrow 2\text{NO}$, colorless nitric oxide, 2315°C .
- (2) $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$, red-brown nitrogen dioxide, below 620°C .
- (3) $3\text{NO}_2 + \text{H}_2\text{O} \rightarrow 2\text{HNO}_3 + \text{NO}$

The NO is not lost for it reacts with oxygen of excess air as in equation (2) above.

The arc process operates in nature. Lightning flashes cause thermal reaction of oxygen with nitrogen, and yearly there is formed nearly 1600 pounds of nitric acid over each square mile of the earth.

The Ostwald Ammonia Oxidation Process. The essential supplement to the Claude-Haber method of making ammonia from its elements is Ostwald's oxidation of ammonia to nitric acid. The following equations give the steps:



Ammonia mixed with ten times its volume of air is passed through a gauze of platinum wire which catalyzes the reaction, with 95 per cent conversion at about 800° . Contact of less than 0.01 second (perhaps 0.001) is sufficient. The reaction is exothermic and the right temperature is maintained by a stream of cooling water and by regulating the flow of the gases. As with the arc process the fundamental idea had been known a long time but it took an Ostwald to apply it successfully.

The platinum gauze, 80-150 mesh, alloyed with a little rhodium, is made of wires 0.001 to 0.003 inch in diameter (about 0.065 mm.). It becomes more efficient with use and at the same time shows a change to a very rough surface. All of our nitric acid is now made by the ammonia oxidation process except under stress of war demands.

Properties of Nitric Acid. Anhydrous nitric acid is a colorless liquid with a density of 1.52 and a boiling point of 86° . As stated before, it slowly decomposes and develops a red-brown color from dissolved oxides of nitrogen.

The constant-boiling mixture forming at 120.5° , with density 1.4, contains 68 per cent HNO_3 . As a powerful oxidizing and nitrating agent it is very important.

1. Action on Non-metals. Sulfur heated with nitric acid is oxidized to the trioxide and, in the presence of water, to sulfuric

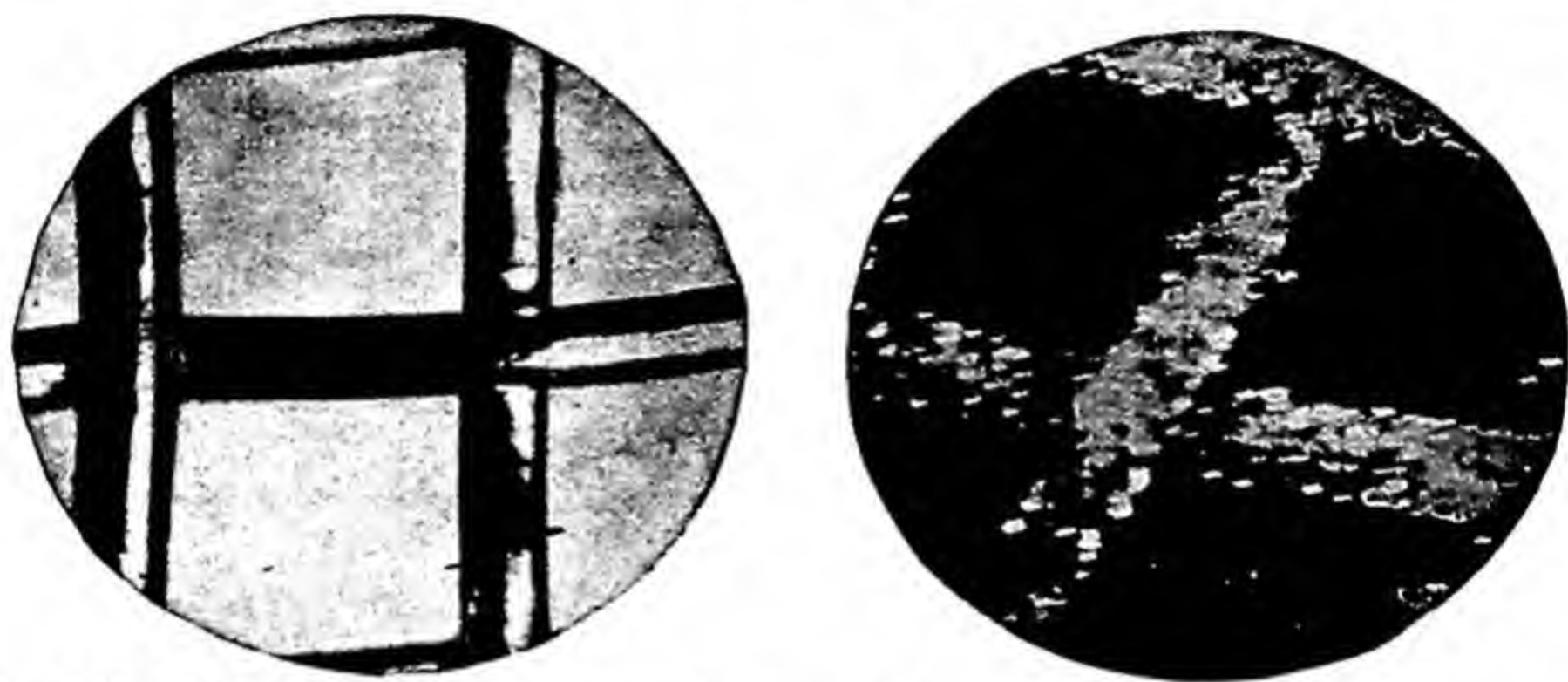


Fig. 119. Platinum gauze before and after use in the catalytic oxidation of ammonia.

acid. In fact by this treatment combined sulfur is torn out and converted into sulfuric acid. This is the basis of quantitative methods of determining the percentage of sulfur in ores and in some foods.

2. Action on Metals. Very active metals displace hydrogen from this acid, but in most cases the hydrogen displaced is instantly oxidized by the acid and none escapes.

Less active metals, such as copper, are first converted into the oxide by the acid, which then dissolves the oxide. If it were not for this preliminary oxidation, nitric acid could not possibly attack metals below hydrogen in the electrochemical series.

3. Action on Metallic Oxides. Oxides react readily with nitric acid, forming water and nitrates.

4. Action on Organic Compounds. Cellulose (of cotton or wood) is attacked with the formation of various cellulose nitrates,

some of which are high explosives. With glycerine a similar product called *nitroglycerine* is produced. Toluene yields the famous T.N.T. (*trinitrotoluene*) and even starch is nitrated to form a powerful explosive. Yellow stains on the hand may be due to the xanthoproteic acid formed by nitric acid reacting with protein tissue.

The gas volume resulting from an explosion of T.N.T. is 2360 times the volume of the solid. A 75-mm. shell contains several explosives; detonator, propellant (smokeless powder), tetryl, T.N.T., etc.

Nitro Compounds and Organic Nitrates. Concentrated nitric acid reacts with organic compounds in two ways, as is well illustrated by its reaction with glycerine and with benzene.

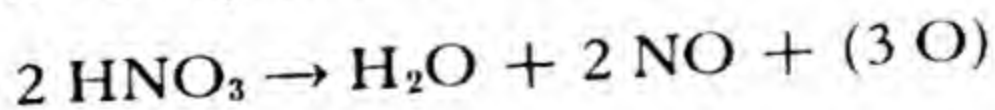


The product, $\text{C}_3\text{H}_5(\text{NO}_3)_3$, is wrongly called "nitroglycerine." The NO_3 group is present, so the correct name is glyceryl trinitrate. The reaction includes the union of OH groups of the glycerine with H groups of the acid.



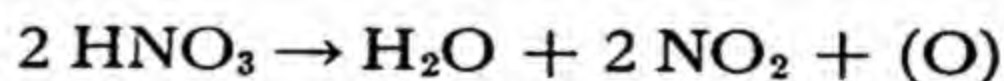
Here it is the benzene, C_6H_6 , that furnishes the H, and the nitric acid (written above as $\text{HO} \cdot \text{NO}_2$ for convenience) that furnishes the OH group for reaction to yield water. The product, $\text{C}_6\text{H}_5\text{NO}_2$, is clearly not a nitrate of any sort, but, since it contains the nitro group $-\text{NO}_2$, must be called nitrobenzene. Cellulose contains OH groups and hence reacts like glycerine. Toluene, $\text{C}_6\text{H}_5\text{CH}_3$, resembles benzene closely and reacts similarly with nitric acid to form T.N.T., trinitrotoluene.

Oxidation by Nitric Acid. In the presence of a reducing agent *dilute nitric acid* breaks up, yielding (to the reducer) three oxygen atoms for every two molecules of the acid:

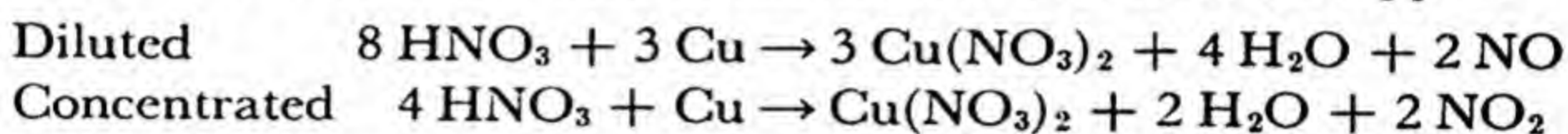


The (O) of the above equation is not set free as oxygen gas but is merely used here for convenience in balancing the equation.

When *concentrated acid* is used, nitric oxide cannot be a product. It would be oxidized to nitrogen dioxide by the rest of the concentrated acid.

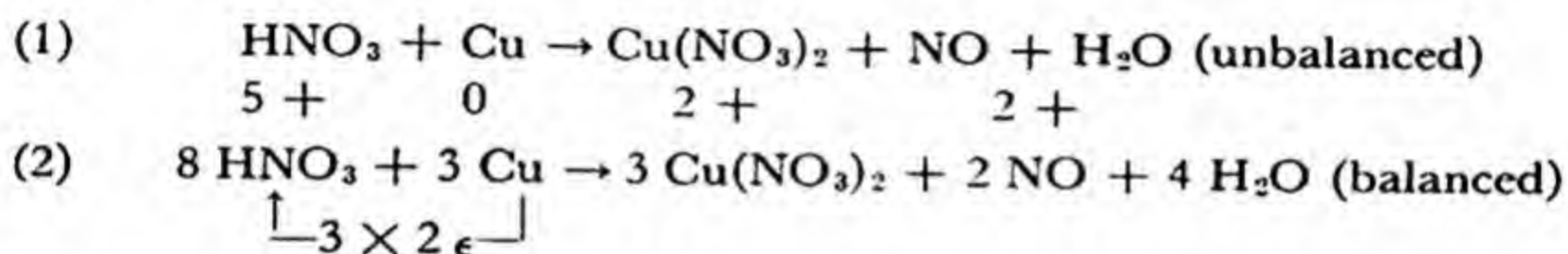


Note again the difference in the oxidizing power of diluted and of concentrated nitric acid as shown towards metallic copper:



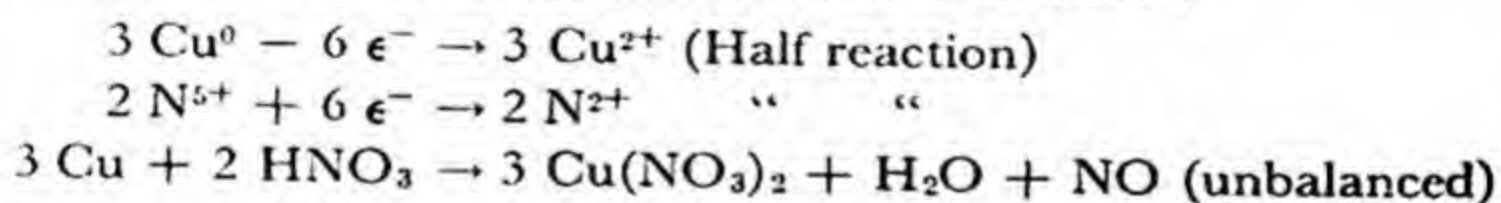
The more active the reducing agent the greater the valence number change in the nitrogen of nitric acid. Silver and sulfur reduce it to NO_2 ; tin to N_2 ; zinc to NH_4NO_3 ; magnesium to NH_4NO_3 and hydrogen. What are these valence number changes in the nitrogen? These reactions occur with concentrated acid diluted with an equal volume of water.

Electronic Balancing of Equations. As an option in balancing these oxidation-reduction equations we may consider again the electron method. Represent electrons by (ϵ).

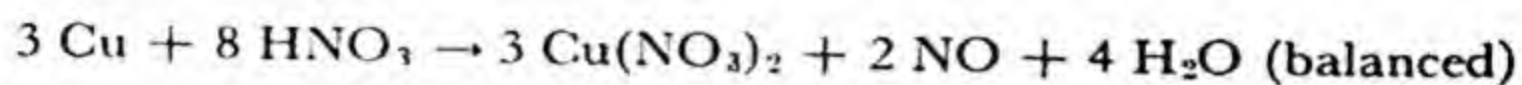


By this method there must be an equal number of electrons (ϵ) gained and lost by the oxidizing and reducing agents. In this instance copper acts as a reducing agent, for its valence is raised from zero to two. Some molecules of nitric acid acted as oxidizing agent and some formed cupric nitrate.

The valence of nitrogen in HNO_3 must be five because the anhydride is N_2O_5 . Another method of representing the reactions is as follows:

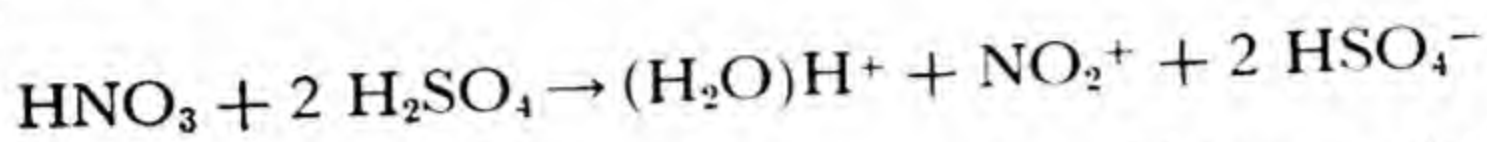


However the six NO_3 groups in $3 \text{Cu}(\text{NO}_3)_2$ require six more molecules of HNO_3 , a total of eight.



9. Add a few drops of nitric acid to a beaker filled with foam from the action of zinc on dilute sulfuric acid. The escape of hydrogen is checked. Pour off the liquid, neutralize with sodium hydroxide, and smell the ammonia released. Explain with all equations.

Doubt has been cast on the theory that vigorous nitration by a mixture of nitric acid with concentrated sulfuric is aided by taking up of water of reaction by the concentrated sulfuric. There is new evidence that the NO_2^+ ion is the effective nitrating agent. The presence of this unusual ion is explained as follows:



Nitrous Acid, HNO_2 . When nitrogen trioxide or a mixture of nitric oxide and nitrogen dioxide is passed into cold water, nitrous acid is formed. The acid is quite unstable, even in solution — so it is stored and transported as sodium nitrite, to be acidified when nitrous acid is desired. When nitrous acid is released from its salts by addition of sulfuric acid, red-brown fumes are seen (unless a great excess of water is present).

Nitrates. All nitrates are soluble except those of mercury (divalent), antimony, and bismuth, which are hydrolyzed with formation of insoluble basic salts. However, these are soluble in the presence of sufficient nitric acid. Why?

Nitrates are grouped in three classes according to their decomposition on heating:

- (1) $\text{NH}_4\text{NO}_3 \rightarrow 2 \text{H}_2\text{O} + \text{N}_2\text{O}$
- (2) $2 \text{NaNO}_3 \rightarrow 2 \text{NaNO}_2 + \text{O}_2$
- (3) $2 \text{Cu}(\text{NO}_3)_2 \rightarrow 2 \text{CuO} + 4 \text{NO}_2 + \text{O}_2$

Ammonium nitrate is the only member of the first group. Potassium nitrate acts like sodium nitrate. Practically all other nitrates are decomposed like lead nitrate (see page 359).

The Brown-Ring Test for Nitrates. A very delicate test for nitrates (and nitrites) makes use of the formation of the brown compound $\text{FeSO}_4 \cdot \text{NO}$. To the suspected nitrate a solution of ferrous sulfate is added and then, while inclining the tube, concentrated sulfuric acid is carefully poured down the wall of the tube so two layers form. At the junction of the two layers a brown ring appears if a nitrate is present. The sulfuric acid liberates nitric acid from any nitrate, which in turn oxidizes some ferrous sulfate. The nitric oxide by-product combines with some remain-

But oxygen is divalent, so the bond of valence once used to hold the hydrogen must exert itself towards something. This suits nitrogen, for its bond of valence previously occupied in holding the third —OH can extend its force to the second oxygen. The same reasoning applies to the fourth and fifth groups. Loss of water is neither oxidation nor reduction, so the valence of the nitrogen remains five and the valence of oxygen two.

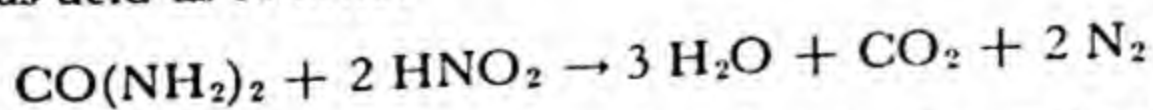
OXIDATION STATES IN GROUP VB

Shown in compounds of N, P, As, Sb, and Bi

	-3	-2	+1	+2	+3	+4	+5
N	NH ₃	N ₂ H ₄	N ₂ O	NO	NCl ₃ HNO ₂	N ₂ O ₄	N ₂ O ₅
P	PH ₃	P ₂ H ₄	H ₃ PO ₂	—	PCl ₃ H ₃ PO ₃	—	P ₂ O ₅ H ₃ PO ₄
As	AsH ₃	—	—	As ₂ S ₂	AsCl ₃ H ₃ AsO ₃	Sb ₂ O ₄	AsCl ₅ H ₃ AsO ₄
Sb	SbH ₃	—	—	—	SbCl ₃		SbCl ₅ H ₃ SbO ₄
Bi	BiH ₃	—	—	BiO		Bi ₂ O ₄	H ₃ BiO ₃

Exercises

- What volume of sulfuric acid having a specific gravity of 1.83 (94 per cent H₂SO₄) will be required to convert 425 kg. of sodium nitrate (80 per cent pure) into nitric acid?
- How many grams of nitric acid will be prepared in the above reaction?
- Assuming a 95 per cent yield, how much Chile saltpeter, 90 per cent pure, would be required to prepare 614 kg. of 68 per cent nitric acid?
- Develop the structural formula of permanganic acid, HMnO₄, and of dichromic acid, H₂Cr₂O₇.
- What possible connection is there between oil shales and fertilizers?
- What is the chief cost in making ammonia directly from hydrogen and nitrogen?
- The white crystalline substance called urea, CO(NH₂)₂, is oxidized by nitrous acid as follows:



How could you arrange apparatus for the determination of the urea in urine? What would be your calculations?

- What process of nitrogen fixation dominates the field?

18. How could you dry ammonia?
19. Compare the action of nitric acid on metals above hydrogen in the electro-motive (or activity) series with the action on metals below hydrogen.
20. How can you tell the difference between a nitrate and a nitrite?
21. How does the fact that cotton or other forms of cellulose can be nitrated touch your own personal safety, comfort, pleasure, or appearance?
22. Is the arc process of making NO completely obsolete?

References

- Hall, W. T., "Oxidation-Reduction Reactions." *J. Chem. Education*, 6, 479 (1929).
- Reinmuth, O., "The Structure of Matter." VII. "Application of the Electronic Theory to Oxidation-Reduction." *J. Chem. Education*, 6, 527 (1929).
- Stoddart, E. M., "The Reaction between Oxygen and Nitric Oxide." *J. Chem. Soc.*, 5 (January, 1939).

Chapter 33 THE PHOSPHORUS GROUP. VB

ELEMENTS	ATOMIC WEIGHT	DENSITY OF SOLID	MELTING POINT	COLOR OF SOLID	HYDROXIDES ARE
Nitrogen	14.008	1.0265	-210.5°	White	Strongly acidic
Phosphorus	30.98	1.83	44.10°	White	Moderately acidic
Arsenic	74.91	5.73	Sublimes	Gray	Moderately acidic
Antimony	121.76	6.684	630.5°	Silver-white	More basic than acidic
Bismuth	209.0	9.80	271°	Reddish-white	Weakly basic

A glance at the Periodic Table shows that the five elements listed above resemble each other in properties. Their place in the table calls for valence numbers of three and five, and these are common except with bismuth, which practically limits itself to a valence number of three. With increasing atomic weights these five elements become more metallic, with all that such a change involves. This change to the basic nature is still more marked with antimony and is complete with bismuth.

The predominant valence numbers of three and five produce a striking similarity in the formulas of compounds.

ELECTRON SHELLS

N, 2, 5	Sb, 2, 8, 18, 18, 5
P, 2, 8, 5	Bi, 2, 8, 18, 32, 18, 5
As, 2, 8, 18, 5	

All the hydrides are gases although only one, NH_3 , reacts with water to form a base. All the chlorides, or other halides, are

hydrolyzed by water, yielding hydroxides which are more or less acidic.

PHOSPHORUS

Occurrence. The element is too active chemically to be found free, but as phosphorite ($\text{Ca}_3(\text{PO}_4)_2$), a fossil deposit, which unfortunately contains some calcium fluoride, it is plentiful in the United States and North Africa. Apatite ($3 \text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaF}_2$), a primitive rock, occurs in large deposits in Canada and Russia.

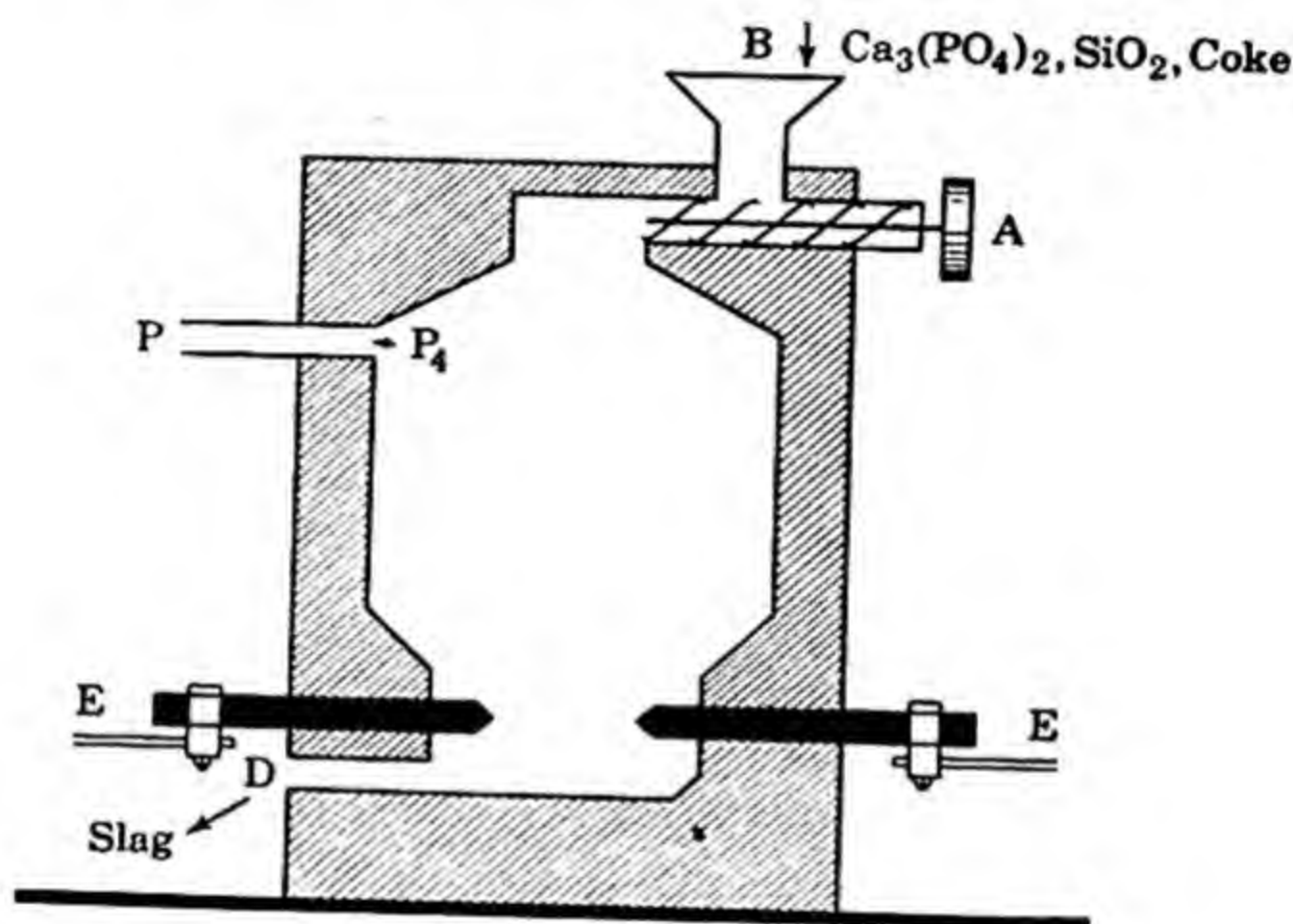
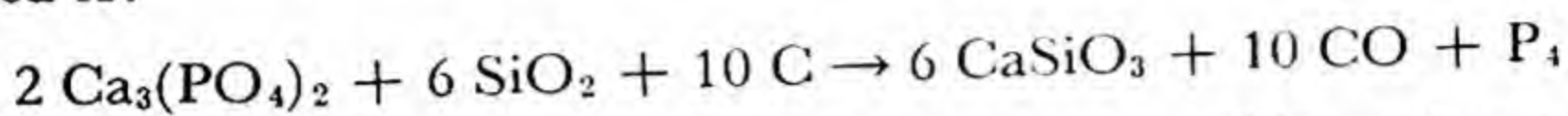


Fig. 120. Phosphorus furnace.

Some iron ores contain very appreciable amounts of phosphates. The average human body contains 1.5 kg. of combined phosphorus, most of which is contained in the bones. The hard part of bones is calcium phosphate, and organic phosphorus compounds are found in nerve tissue, muscles, and in the germs of seeds. Consequently the element is essential to animal and plant growth. Egg-yolk and beans are especially rich in organic phosphorus compounds, but peas and whole wheat are also valuable sources. Since they are a part of plant and animal tissue, it is evident that phosphates must be present in all fertile soils.

Preparation. The modern method of preparing phosphorus is to heat phosphate rock with sand and coke in the electric furnace (Fig. 120). The charge enters the furnace from *B* by the worm feed *A*:



The phosphorus distills off at *P* and is condensed in cold water. After filtering, it is molded into small sticks and kept under water.

Exercise

1. Why not heat phosphate rock, sulfuric acid, and coke together to make phosphorus cheaply?

Properties. Phosphorus exists in at least three allotropic forms—white, red, and black—thus reminding us of oxygen-ozone and the different forms of sulfur.

The transformation from white phosphorus to red involves a change in specific gravity from 1.83 to about 2.34 and, because much heat is liberated, there must be less energy in the red form. This explains why the heat of combustion of the red phosphorus is less. On burning, each variety produces a dense white smoke of solid P_2O_5 . Military smoke screens have been made this way. Colored signal smokes are made by ignition of a mixture of milk sugar, a dye, and potassium chlorate.

White Phosphorus. White phosphorus is a translucent, waxy solid, melting at 44° and boiling at 287° . Its density is 1.83 at room temperature. From the density of its vapor it is found that up to 1500° the molecule is P_4 and at 1700° it is P_2 . Insoluble in water, it is soluble in carbon disulfide, turpentine, ether, olive oil, and other liquids. From these solvents it crystallizes in the regular system. It is extremely active and combines with many elements. In warm air it ignites (at about 35°), so it is always kept under water. The heat of the hand is sufficient to ignite it and serious burns may result. This form of the element is very poisonous, a fatal dose being only 0.15 g.

2. What was said about phosphorus in connection with ozone and also in connection with iodine?

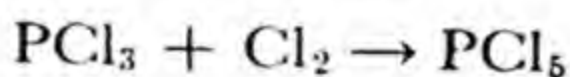
Red Phosphorus. When white phosphorus is heated to 230° – 300° without access of air it changes to the red modification—more rapidly in the presence of a trace of iodine as a catalyst. Red phosphorus is not soluble in any solvent, is non-poisonous, and must be heated to about 240° before it takes fire. It is micro-crystalline.

Matches. Friction matches first came into general use in 1827, adding a great deal to comfort and convenience. We use 500 billion yearly. Heat of friction was secured by the use of powdered glass on the box, and ready combustion was secured by use of phosphorus, a sulfide and solid oxidizing agents glued together in the head. Later the non-toxic P_4S_3 was substituted for white phosphorus which had caused a serious disease of the bones in workers making the matches.

In the safety match, red phosphorus and glass powder are glued to the box with the other necessary materials, sulfur or antimony trisulfide, potassium chlorate and glue, in the head. The head and the box coating must cooperate.

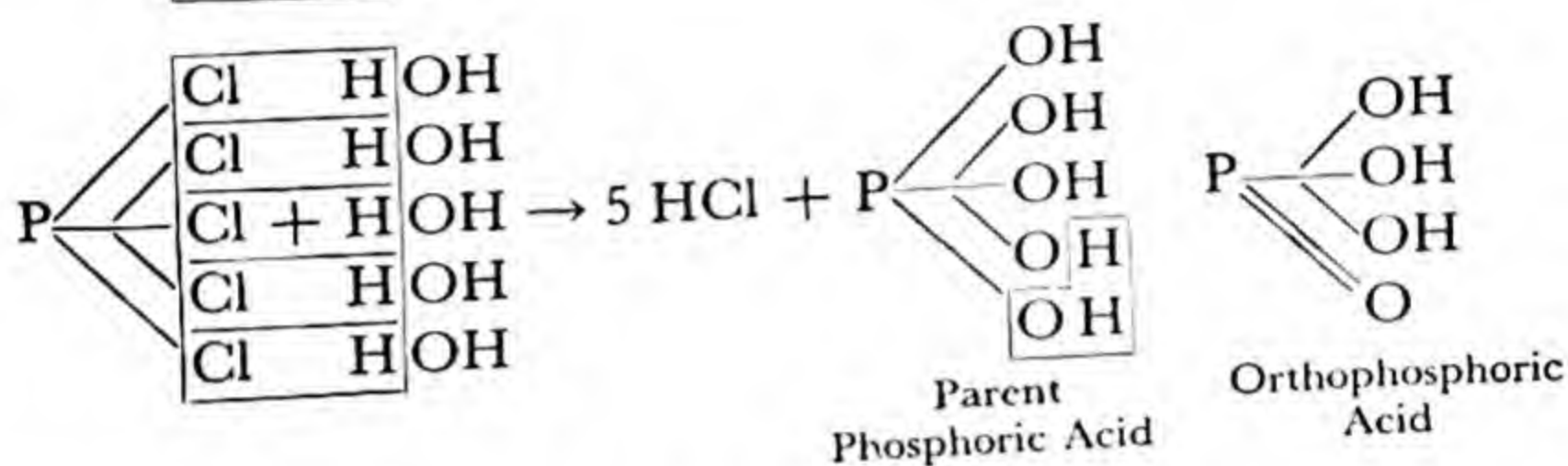
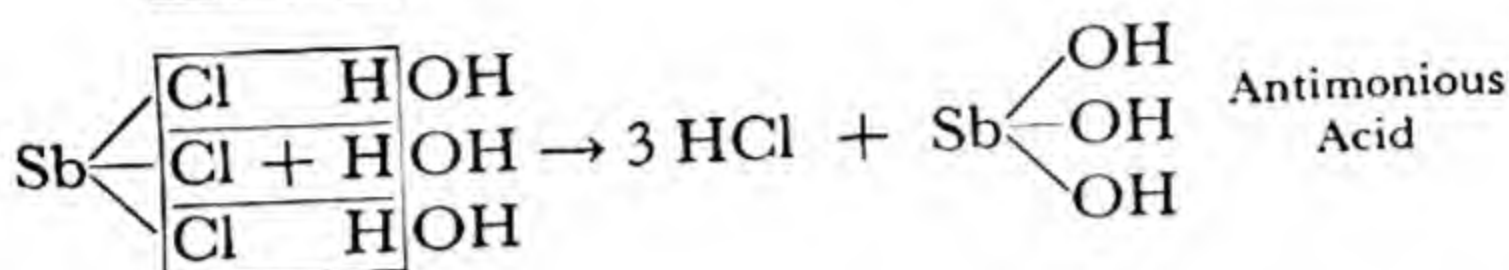
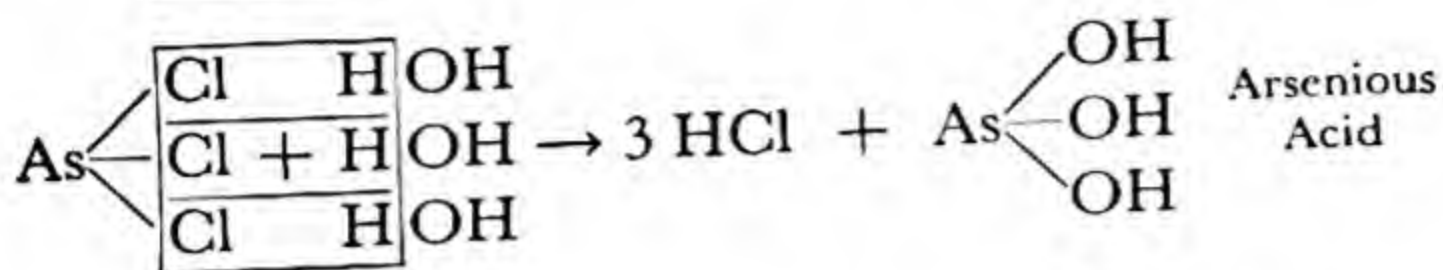
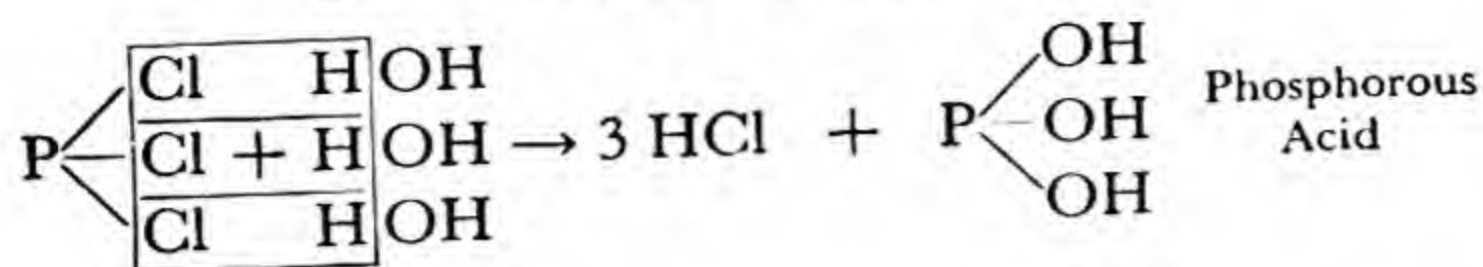
Other Uses. Normally most of the phosphorus produced goes into the match industry in the red form or as the sulfide. A small amount is used as a rat poison and in modern warfare much is used in incendiary grenades or bombs and to make smoke screens of the pentoxide.

Chlorides. Phosphorus reacts with chlorine, even in the cold, to form the trichloride (PCl_3), a colorless fuming liquid of density 1.6, and the pentachloride (PCl_5), a pale yellow solid. Passing more chlorine through the trichloride converts it into the pentachloride, with evolution of much heat:

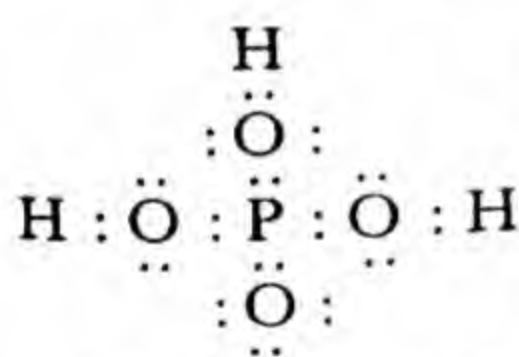


Oxides. Of the two oxides, P_2O_3 and P_2O_5 , only the latter is important. They are white solids, anhydrides of phosphorous and phosphoric acids.

The Acids of Phosphorus. A study of the hydrolysis of the chlorides of phosphorus and of the other elements of the group is of the utmost importance in giving the student a clear conception of the formulas of the acids:

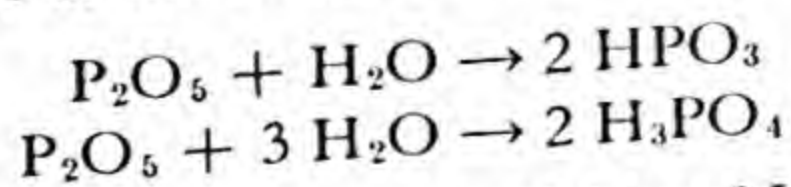


3. Write the similar reactions of AsCl_5 and SbCl_5 .



This graphic formula for H_3PO_4 shows the completion of the outer octet shell of valence electrons in the atoms of phosphorus and oxygen.

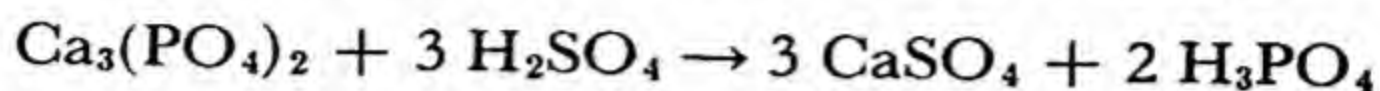
Orthophosphoric Acid. All the acids of pentavalent phosphorus, in aqueous solution, slowly revert (by hydration) to orthophosphoric acid. The pure acid can be made by reaction of water with phosphorus pentoxide. At first metaphosphoric acid (HPO_3) forms but slowly (more rapidly if a little nitric acid is added as a catalyst), this acid adds more water, and the orthophosphoric acid (H_3PO_4) results. In other words the pentoxide is the anhydride of the ortho-acid:



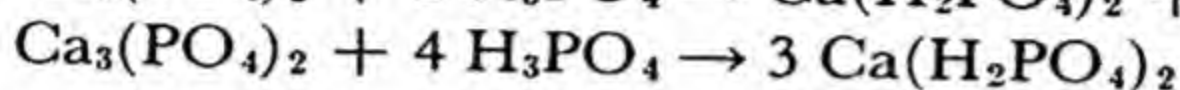
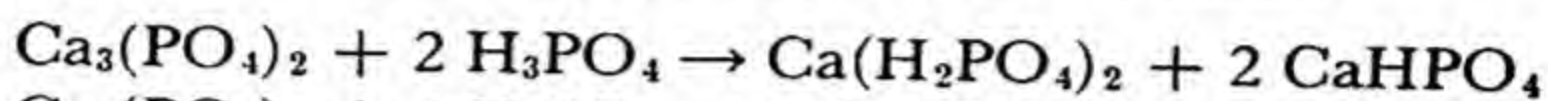
Obviously it is also the anhydride of HPO_3 .

Commercial phosphoric acid, a thick syrupy liquid of about 85 per cent concentration, is cheaply made from phosphate rock by somewhat diluted H_2SO_4 . A purer product results from direct action of water on P_2O_5 .

With excess of phosphate rock the first reaction



may be followed by either of the following, depending upon the amount of this excess and the dilution of the acids:



Some phosphoric acid is made in a blast furnace, much as iron is reduced from its oxide ores, but the electric furnace is better.

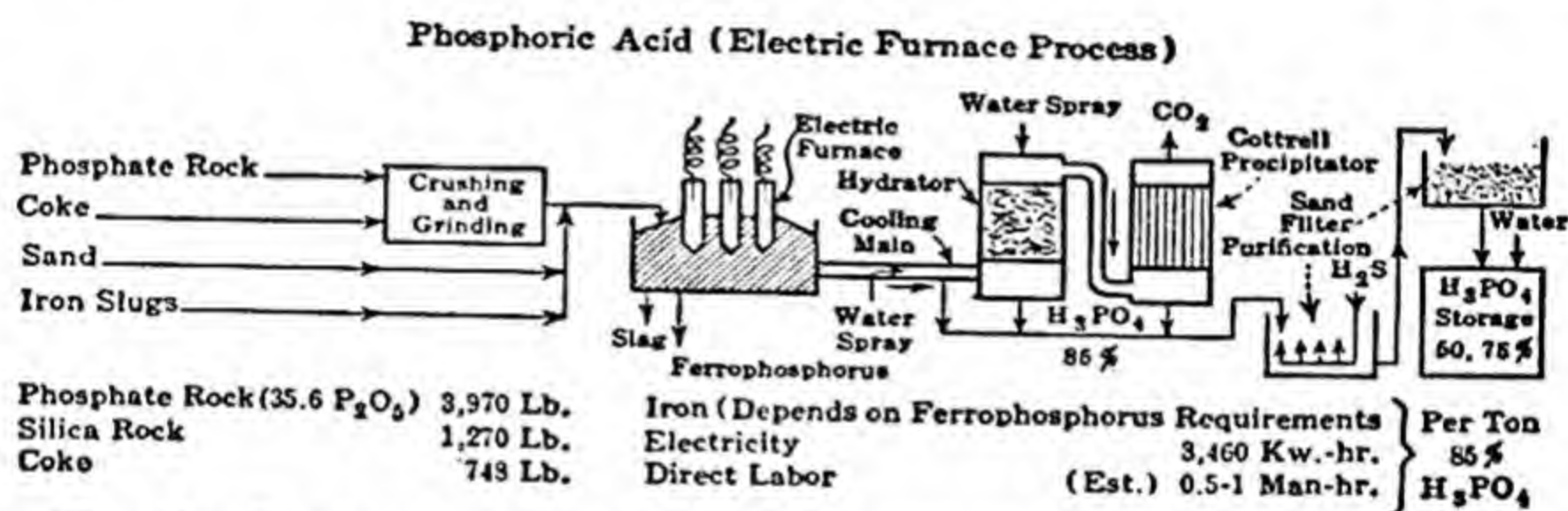
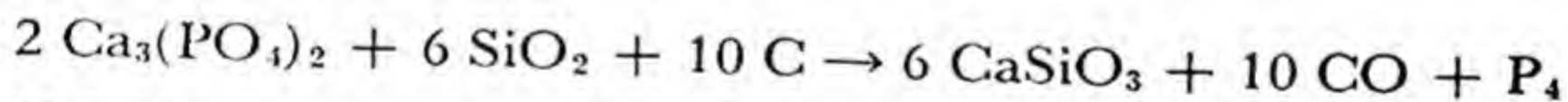


Fig. 121. Flowsheet of electric furnace process of making phosphoric acid.
(Courtesy Chem. Met. Eng.)

Phosphate rock is not an oxide, it is a calcium phosphate requiring the aid of silicon dioxide (which at high temperatures acts like an acid) for removal of calcium. Summing up the various reactions:



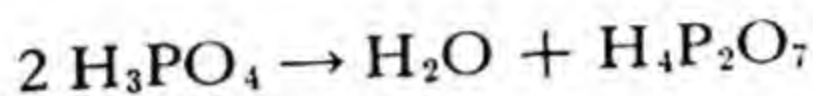
Coke in the electric or blast furnace reduces the rock (with the aid of silicon dioxide) to elementary phosphorus. The gases may be led through a cooling system where phosphorus is condensed (if the market demands it) or mixed with more air so that the element burns to the oxide, P_2O_5 . The oxide is then hydrated to yield H_3PO_4 , orthophosphoric acid, in the form of a mist which

must be settled and condensed by the aid of the Cottrell electrical precipitation device. Fluorine in the rock goes into the slag as calcium fluoride.

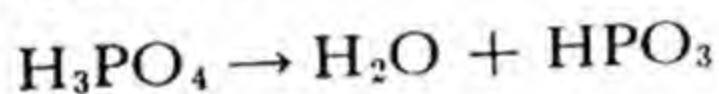
A quick treatment of sheet steel by phosphoric acid plus a suitable catalyst forms a rough, rust-proof surface very suitable as a base for lacquers. All steel auto-bodies are treated by this "bonderizing process."

Orthophosphoric acid finds important use as a catalyst in petroleum chemistry.

Pyrophosphoric Acid. This acid, as its name indicates, is the result of heating orthophosphoric acid. At 213° water is lost as follows:



Metaphosphoric Acid. By heating orthophosphoric acid to 400° a greater loss of water results than in the preparation of the pyro acid, and metaphosphoric acid is formed:



It is also the first reaction product when the pentoxide is added to water. The pure dry acid looks like ice and is called "glacial" phosphoric acid.

PHOSPHATES

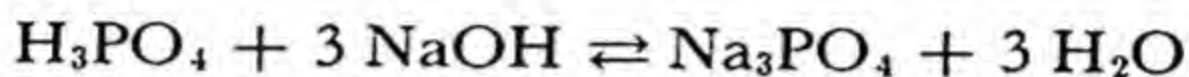
Salts. Sodium salts of phosphoric acid are used in the preparation of fertilizer, in baking powder, water softening, weighting silk, clarifying sugar solutions, rust-proofing of metal, fire-proofing, soft drinks, and in yeast manufacture. Organic phosphates such as tricresyl phosphate are used as softeners in some plastics.

Orthophosphates.

- Na_3PO_4 , trisodium phosphate (the tertiary salt)
- Na_2HPO_4 , disodium phosphate (the secondary salt)
- NaH_2PO_4 , monosodium phosphate (the primary salt)

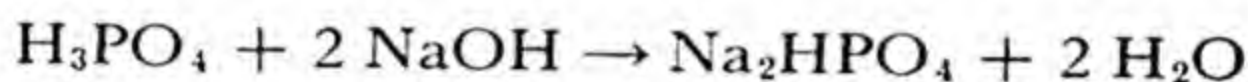
Trisodium phosphate is strongly hydrolyzed to yield an alkaline solution and so is often used as a washing powder. The salt is

easily prepared by adding a large excess of sodium hydroxide to the acid. Thus:



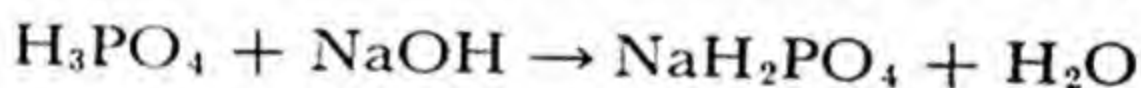
The tendency towards reversal is here so great that it is only by the mass action of a large excess of the base that crystals of the trisodium phosphate can be secured. *Trisodium phosphate*, in boiler-water treatment causes precipitation of insoluble calcium phosphate and magnesium hydroxide.

If phosphoric acid is titrated with sodium hydroxide until neutral to phenolphthalein as an indicator, *disodium phosphate* is formed:



Monocalcium phosphate, CaHPO_4 , is used in some baking powders; dicalcium phosphate in mineral nutrition, ceramics and as a dentifrice base.

Monosodium phosphate, which is used in baking powders, pharmaceuticals, and in boiler-water treatment, is prepared from an equimolecular mixture of the acid and the base:



Its solution is weakly acidic.

The acidic or basic reactions of the orthophosphates should be evident from a comparison of the ionization constants of orthophosphoric acid in its three stages:

$$(1) \quad \frac{[\text{H}^+] \times [\text{H}_2\text{PO}_4^-]}{[\text{H}_3\text{PO}_4]} = 10^{-2}$$

$$(2) \quad \frac{[\text{H}^+] \times [\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} = 10^{-7}$$

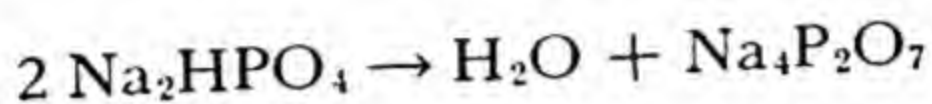
$$(3) \quad \frac{[\text{H}^+] \times [\text{PO}_4^{3-}]}{[\text{HPO}_4^{2-}]} = 10^{-13}$$

Note: 10^{-7} is really $\frac{1}{10^7}$ or 0.000,000,1.

In a very acid solution $\text{Ba}_3(\text{PO}_4)_2$ is not precipitated because ionization of HPO_4^{2-} ion to yield H^+ and PO_4^{3-} is too greatly repressed by excess H^+ added. Under such conditions the concentration of PO_4^{3-} ions is too minute to help the Ba^{++} ions exceed the solubility product of $\text{Ba}_3(\text{PO}_4)_2$.

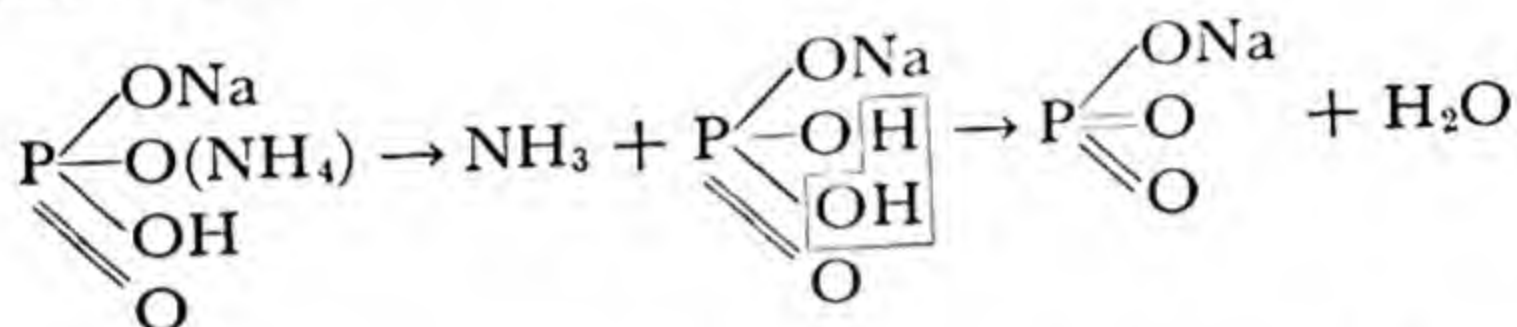
Interesting changes take place on heating the dry salts. If there are two —OH groups in one molecule, they yield a molecule of water. If only one —OH is found in a molecule of the salt, then two molecules must get together in order to make the loss of water possible.

An orthophosphate can be changed into a pyrophosphate by heating:

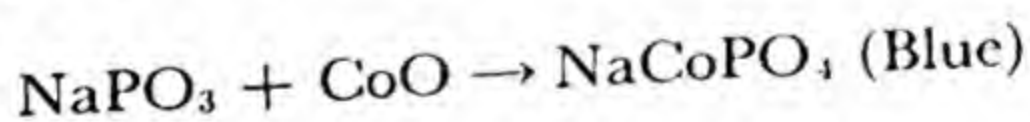


This $\text{Na}_4\text{P}_2\text{O}_7$, called tetrasodium phosphate, has large use in soaps, in degumming silk, and in oil well drilling muds.

Below, an orthophosphate (microcosmic salt) is changed to a metaphosphate:



“Microcosmic salt” is used in bead tests to detect the presence of certain salts. When heated in a loop of platinum wire the salt loses water of crystallization and also ammonia gas as shown above. A metaphosphate results. The glassy bead is then touched to the substance to be tested and heated again. If a cobalt salt is tested, some oxide is probably formed by the hot flame, and this oxide unites directly with the sodium metaphosphate of the bead to form an orthophosphate of sodium and cobalt. This is intensely blue and is characteristic of cobalt, hence a test for it:



Ammonium phosphate fireproofs textiles and wood by releasing NH_3 when heated.

4. Start with the element and show how to make from it all three acids of pentavalent phosphorus.
5. Start with phosphorus pentoxide and make an orthophosphate. From this make a metaphosphate. From this make an orthophosphate again.

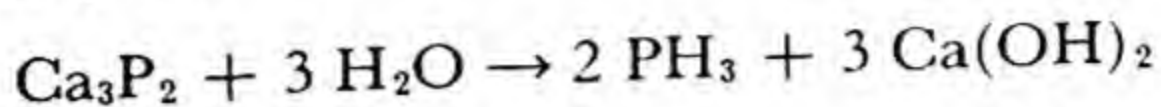
Hexametaphosphates. By heating disodium phosphate for an hour or more at a red heat and quickly cooling, a glassy product known as sodium hexametaphosphate is obtained. It seems to be $(\text{NaPO}_3)_6$ and has unique and valuable properties in that it forms soluble complex calcium and magnesium salts which yield such low concentrations of simple calcium ions, for example, that addition of oxalate ions fails to precipitate the extremely insoluble calcium oxalate. Hard water properly treated with sodium hexametaphosphate will not precipitate wastefully and unpleasantly the usual calcium and magnesium soaps. The calcium is present in a complex anion and not as a simple cation.

There are other complex phosphates related to "hexametaphosphate," some of them crystalline. One of them greatly shortens the time required for vegetable tanning of leather, and improves the quality of leather.

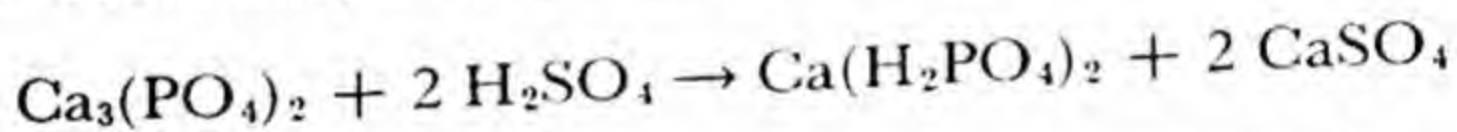
Tests for the Different Phosphates. A neutral solution of an orthophosphate reacts with silver nitrate to form yellow silver phosphate. A solution of pyrophosphoric acid reacts with zinc acetate to yield a white precipitate of zinc pyrophosphate. The other phosphates do not.

White precipitates of silver pyrophosphate and silver metaphosphate leave us uncertain as to which salt we are testing. However, a solution of egg albumin is coagulated by metaphosphoric acid, while the other acids have no such effect. Note that the tests with silver nitrate must be made on solutions of the salts, and that the albumin test must be made with the free acids. If salt solutions are at hand, addition of acetic acid will liberate enough of the phosphoric acids. Nitric acid solutions of orthophosphates form a yellow precipitate when warmed with ammonium molybdate. The formula is too intricate for us in this beginning course. With a mixture of magnesium chloride, ammonium chloride, and ammonium hydroxide (magnesia mixture) a white precipitate of magnesium ammonium phosphate (MgNH_4PO_4) forms. These two reactions are the basis of the best methods of quantitatively determining the phosphorus in fertilizers, etc. Precipitates of exactly the same appearance and similar formula are obtained with orthoarsenates.

Phosphine. This poisonous gas, PH_3 , formed on moistening Ca_3P_2 , reminds us of NH_3 , AsH_3 (poisonous arsine), and SbH_3 (stibine)—all gases.



Phosphate Fertilizers. Since plants contain phosphorus compounds, soils must contain phosphates or must be fertilized properly. Although fertile soils actually contain such compounds heavy cropping finally exhausts the supply and phosphates must be added. Of course plants can utilize only soluble phosphates, so the common practice is to heat ground calcium phosphate rock with enough sulfuric acid to form the soluble primary calcium phosphate (only one hydrogen of each molecule of the acid replaced by a metal), or as it is called commercially, "superphosphate," containing 20 per cent P_2O_5 :



Harmful fluorine is removed as hydrogen fluoride. Soil acids can slowly convert the raw phosphate rock into soluble phosphates but the fluorides would not be removed.

A triple superphosphate concentrate has been made by mixing 78 per cent H_3PO_4 from the electric furnace with ground rock phosphate, storing for several weeks, and grinding to size of powder desired.

If the phosphorus pentoxide coming directly from a phosphorus burner is brought into contact with hot phosphate rock, molten calcium metaphosphate of fertilizer grade is formed.

The world uses 11,000,000 tons of phosphate rock yearly and the United States usually produces about one-half of this total, and exports one million tons. In America, Florida produces two-thirds of the present output, but Tennessee, South Carolina, and Montana also yield large amounts. The largest deposits in the world are found in Utah, Montana, Wyoming, and Idaho, where government investigations report at least 6,000,000,000 tons of 30 per cent calcium phosphate in sight. Since our southern de-

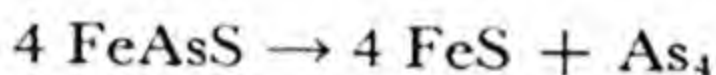
posits will be exhausted in a century, it is reassuring to learn that this western deposit will supply our needs for several centuries.

6. Would you expect to get hydrogen sulfide by treating phosphorus sulfides with dilute acids? Why?

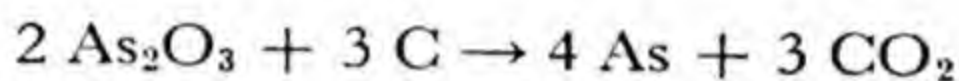
ARSENIC

Occurrence. Arsenical pyrites or mispickel (FeAsS) is abundant, and there are also deposits of the trioxide, orpiment (As_2S_3), realgar (As_2S_2), and arsenides of iron, nickel, and cobalt. Arsenic occurs in some sulfide ores, such as those of copper, and thus its oxide is found in flue dust from the smelters. Canadian arsenic is chiefly derived from the silver-cobalt-nickel arsenides of the cobalt district.

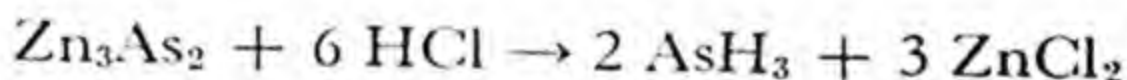
Preparation. Much arsenic is made commercially by heating arsenical pyrites:



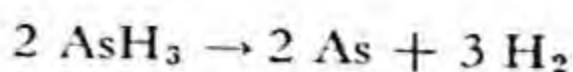
In the laboratory, reduction of the trioxide by hot carbon is an easy method:



Arsenides react with water or, more rapidly, with acids to form arsine. This is similar to the action of nitrides and phosphides on water:



The famous Marsh test for arsenic is based on reduction by active hydrogen. A flask (Fig. 122) containing a frothing mixture of pure zinc and sulfuric acid is connected with a glass tube constricted at two points. Through a funnel a solution of the suspected arsenic compound is added. The poisonous arsine formed on reduction by active hydrogen is heated as it passes through the delivery tube and the element is deposited farther along as a shining mirror. It is best worked so that the mirror forms in a constriction. As little as one-millionth of a gram of arsenic can be detected in this way, so it is a famous test in poisoning cases. An interesting variation is to light the hydrogen as it issues from the delivery tip and to hold a porcelain dish in the flame. The heat of the flame decomposes arsine in the middle of the jet and a shining black spot of the element forms on the cold dish.



A similar reaction occurs in the hydrogen sulfide flame and with SbH_3 , stibine. Arsenic is highly toxic, a fatal dose being only 30 mg.

Arsenic poisoning is now less dangerous because, in the search for a remedy for injury by lewisite (war gas), it was found that 2,3 dithiopropanol (BAL) actually removed arsenic from the body.

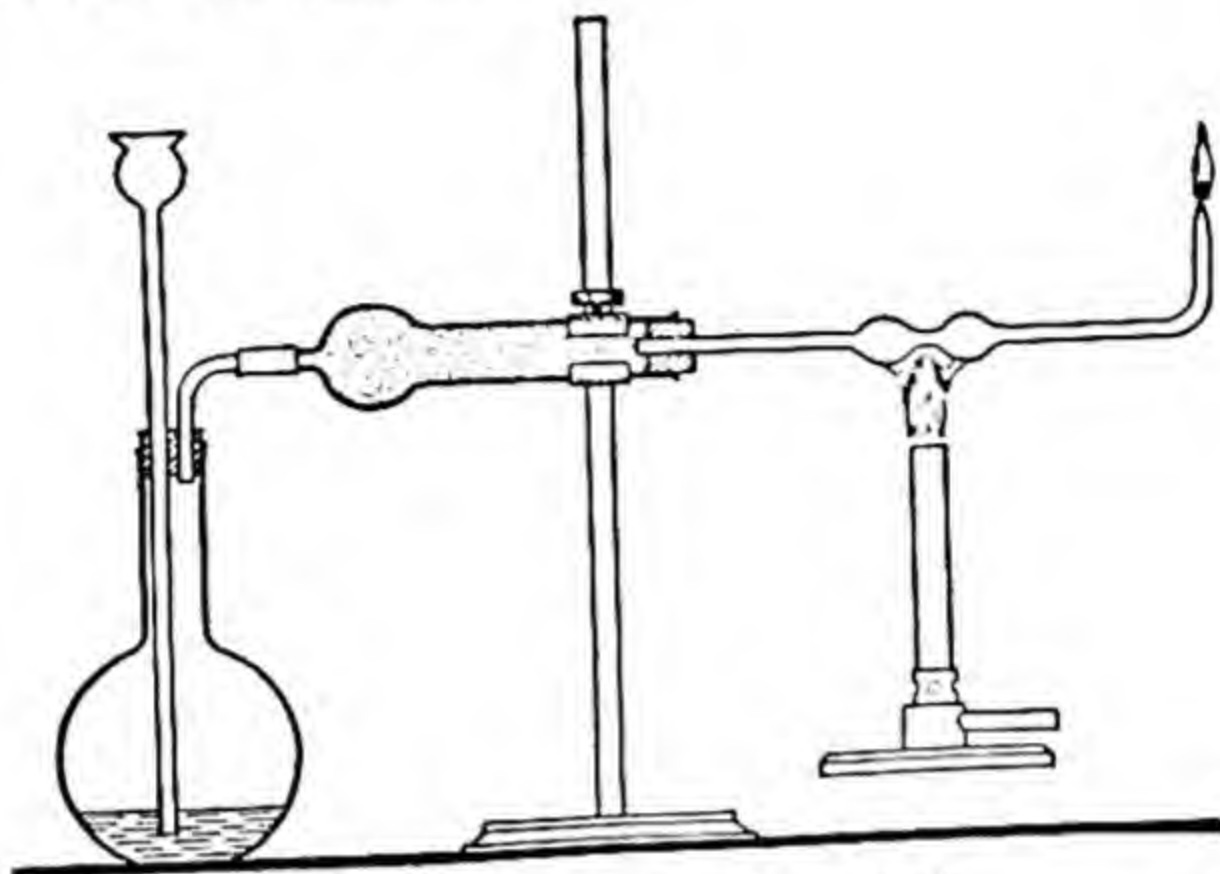


Fig. 122. Marsh test for arsenic.

Properties. In physical properties arsenic resembles the metals, but chemically it is a non-metal, and acid former. Like another member of this group, phosphorus, it exists in allotropic forms.

The common form is gray, brittle, has a specific gravity of 5.727, and volatilizes on heating. (When a solid passes into vapor without melting, it is said to sublime.) Like other solids that sublime, it can be melted under pressure. Sublimation affords an easy method of purifying. The vapors have a strong garlic odor. The element burns in air, forming a white smoke of the trioxide.

Uses. The element is used commercially in alloys as a hardening agent, notably in lead shot.

The trioxide (As_2O_3), a white powder, is electrically precipitated from the flue gases of some smelters using sulfide ores.

Fully 57 per cent of arsenic oxide production goes into insecticides and 30 per cent to weed killers. Some is used for wood preservatives and some in the glass industry. This country usually produces about 20,000 tons and imports more.

Insecticides are important, considering that our crop losses due to insect pests total \$2,000,000,000 yearly.

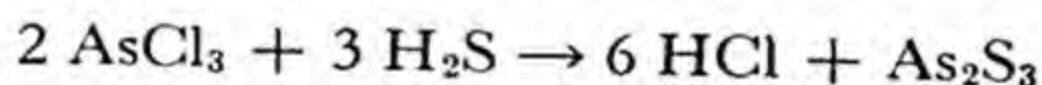
The ammunition for attack on insect enemies (and fungi) in the United States includes:

Lead aresnate	45,000,000 pounds
Calcium arsenate	70,000,000
Sulfur dust	30,000,000
Lime-sulfur	43,000,000
Arsenic trioxide (for grasshoppers)	1,000,000
Paris green	3,000,000

This great addition of material to fruits, vegetables, and soils is alarming and has produced legal restrictions as to the permissible amounts on apples, etc., sold in the market.

Acids of Arsenic. As with nitrogen and phosphorus, so there are two types of acids of arsenic, those of trivalent arsenic and those of pentavalent arsenic. The derivation and naming are similar.

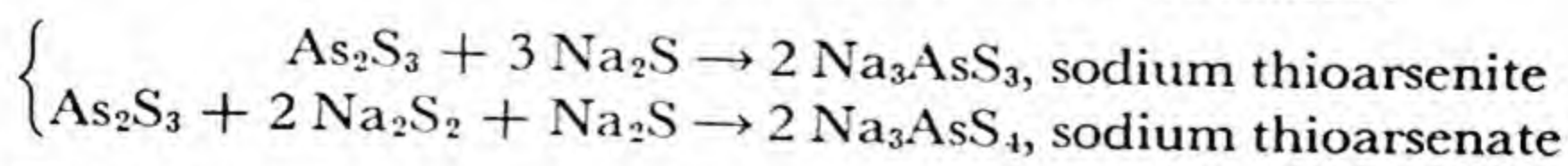
The Sulfides. Solutions of compounds of trivalent arsenic react with hydrogen sulfide to precipitate yellow arsenic trisulfide:



Compounds of pentavalent arsenic react slowly, even when kept almost boiling, to yield mixtures of yellow arsenic pentasulfide, the trisulfide, and sulfur. Both sulfides are oxidized by hot concentrated nitric acid to arsenic acid with release of sulfur. With prolonged action the sulfur may become sulfuric acid.

The sulfides of the sodium group react with arsenic trisulfide to form soluble salts.

The Thio-Acids and Salts. On warming arsenic trisulfide with sodium sulfide (ammonium sulfide is often used with similar results) a soluble salt is obtained. If sodium polysulfide (Na_2S_2) and some Na_2S are used, a different soluble salt is obtained:



The formulas of these salts remind us of Na_3AsO_3 , sodium arsenite, and Na_3AsO_4 , sodium arsenate. The difference is merely the presence of sulfur in place of oxygen. The name thio- is then prefixed to the usual name.

When solutions of these soluble and reasonably stable thio-salts are acidified, we might expect to get, at least in equilibrium, the free thio-acids from which the salts were derived. But precipitates of the sulfides are obtained. The explanation is simple. The thio-acids are indeed liberated, but decompose at once with loss of hydrogen sulfide (much like spontaneous loss of water from —OH groups in oxygen acids) and the simple insoluble sulfides are left:

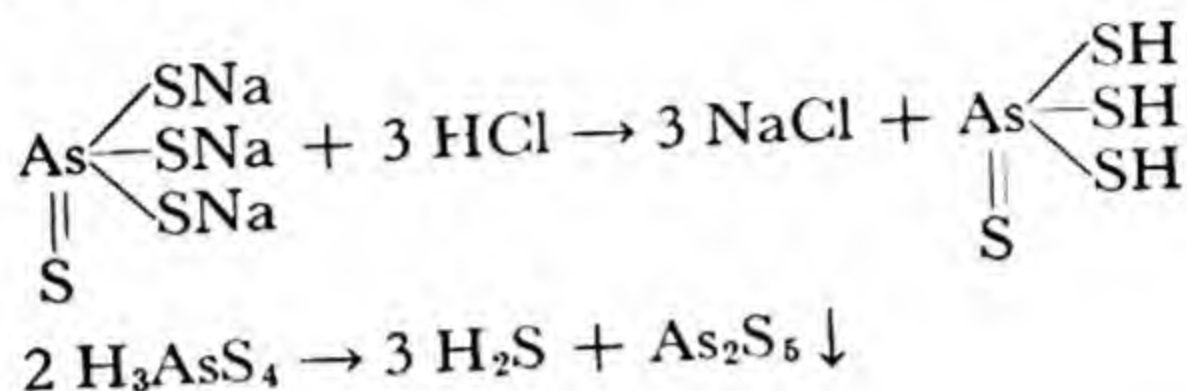


Diagram the reactions of acid on Na_3AsS_3 .

It is important to note that warming arsenic trisulfide with plain sodium sulfide (Na_2S) does not change the valence of the arsenic, does not oxidize it. But warming with sodium polysulfide (Na_2S_2) gives us a thio-salt (Na_3AsS_4) in which the arsenic has a valence of five, and on decomposing this compound with an acid arsenic pentasulfide results. The extra sulfur in the sodium polysulfide in effect adds on to the arsenic, giving it the full valence of five. These reactions are of the utmost importance in qualitative analysis.

Sulfides of antimony and tin in the higher valence states are less basic or more acidic than the lower sulfides, and therefore dissolve readily in ammonium sulfide.

ANTIMONY

History. Antimony, or perhaps its sulfide, was used as a medicine or cosmetic in the Orient before the Christian era. By the close of the eighteenth century the chemistry of antimony was much better known than that of any other element.

Occurrence. Although found free in small quantities, the element is found chiefly as the sulfide (Sb_2S_3). China practically supplies the world's annual need of 23,000 tons, with Mexico and the United States producing some.

Preparation. The sulfide "stibnite" is reduced by heating with scrap iron:



By another method the sulfide is melted away from the gangue or common rock in the ore and is then roasted into the oxide which is reduced by hot carbon.

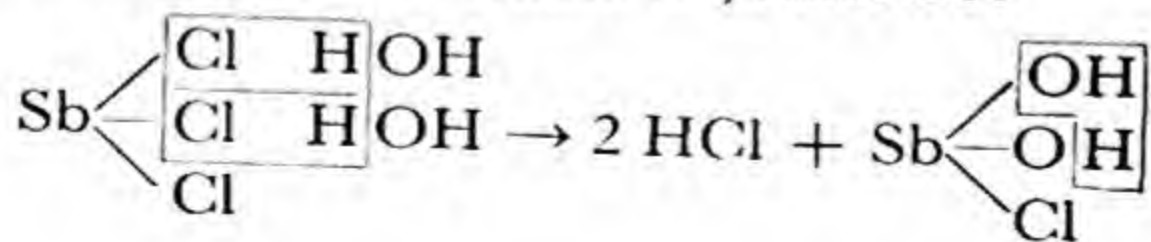
Properties. The change from the non-metallic nature of nitrogen and phosphorus is noticeable in arsenic, but with antimony it becomes decided. This element reacts with sulfuric acid to form a sulfate of antimony. Here the element plays the part of a metal. Yet it is unlike the metals in that it is a poor conductor.

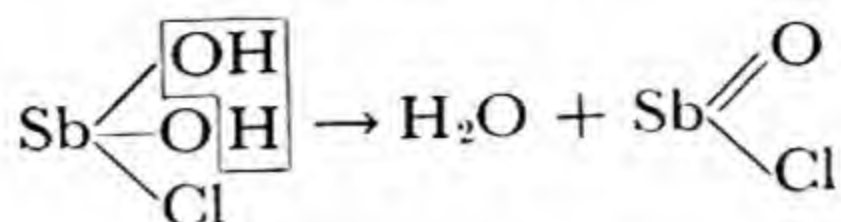
Antimony is a silver-white, brittle element, melting at 680° , and boiling at 1440° . Its specific gravity is 6.7. It expands slightly on cooling from the liquid to the solid state. Only the oxidizing acids attack it and these may form insoluble oxides. In qualitative analysis it is convenient to remember that antimony and tin are the only metals converted into such insoluble oxides by concentrated nitric acid. Antimony reacts readily with phosphorus, arsenic, sulfur, and the halogens.

Uses. Its chief value is in making alloys, such as type metal, lead-antimony grids for storage batteries, bearing metals, and others. Its property of expanding on cooling makes it essential to type metal, for a sharp imprint of the type is desired.

Salts. Antimony nitrate ($\text{Sb}(\text{NO}_3)_3$), as well as the sulfate ($\text{Sb}_2(\text{SO}_4)_3$), is almost completely hydrolyzed, which shows that the hydroxide of antimony is a very weak base. When the trioxide is boiled with potassium hydrogen tartrate ($\text{KHC}_4\text{H}_4\text{O}_6$) tartar emetic is formed. Its formula, $\text{K}(\text{SbO})\text{C}_4\text{H}_4\text{O}_6$, shows that one hydrogen of the acid salt is replaced by the antimonyl group ($\text{SbO}-$). Other salts in which this group acts like a metal are known. This particular salt is used in medicine and as a mordant in making certain fabrics take up dyes.

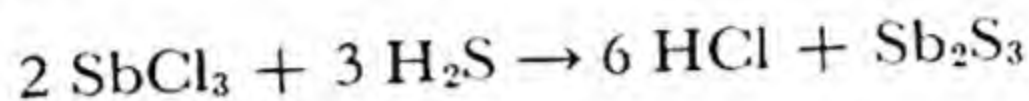
The trichloride is hydrolyzed to the basic chloride, which then loses water, forming the insoluble oxychloride:





7. How could you change from KH_2SbO_4 to potassium metantimonate?

Sulfides and Thio-Salts. Freshly precipitated antimony trisulfide is orange-red, although when melted it is black like the mineral stibnite:



It dissolves in alkaline sulfides like arsenic sulfide. Instead of thioarsenic acid we refer to thioantimonic acid, etc. The oxidation relations are the same, and spontaneous decomposition of the thio-acids with precipitation of simple sulfides follows the same rules. Write all the formulas and reactions that are given under thio-compounds of arsenic with the substitution of Sb for As and they will be correct. See page 384.

BISMUTH

Occurrence. Bismuth is much scarcer than the other members of this group. The element is found free and also as the sulfide (Bi_2S_3), oxide (Bi_2O_3), and the telluride (Bi_2Te_3). Bismuth is now obtained chiefly from anode slimes in the electrolytic refining of copper, lead, and tin. We import only 3000 tons, most of which comes from Peru and Canada.

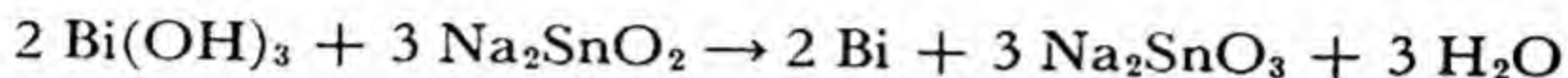
Preparation. Roasting the sulfide ore and then reducing the oxide with hot carbon is a common method of preparation.

Properties. Bismuth is strictly metallic, brittle, and crystalline. In color it is silver-white with a reddish tint. It melts at 271° , boils at 1435° and, although stable in air, will burn to the trioxide (Bi_2O_3). It unites directly with the halogens and decomposes steam at a red heat.

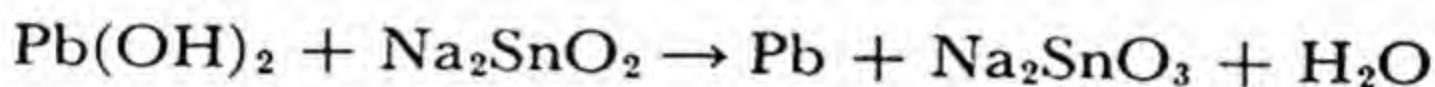
Bismuth may be electroplated on other metals and forms a film capable of taking a high polish. There is little use for the element alone but in very low-melting alloys it is rather important.

Compounds. The trichloride formed by treating bismuth with chlorine or aqua regia hydrolyzes with the precipitation of BiOCl . (See the similar compound of antimony.) The nitrate ($\text{Bi}(\text{NO}_3)_3$) is hydrolyzed very noticeably, producing a salt used in medicine under the name "bismuth subnitrate," $\text{Bi}(\text{OH})_2\text{NO}_3$. Bismuth medicines now rival mercury compounds in treatment of venereal diseases.

Bismuth Test. Salts of bismuth react with alkaline solutions of stannites as shown below. Bismuth hydroxide is first formed:



The similar reaction



is remarkably accelerated, or catalyzed, by traces of bismuth compounds. One part of bismuth in 80,000,000 can be detected by this test. The reduced lead gives a black color to the solution. Tests should be made for comparison with and without the bismuth.

Exercises

8. A certain copper ore contained 1.5 per cent of arsenic. What weight of arsenious oxide could be formed from 211 tons of ore?
9. What volume of phosphine at 30° and 765 mm. will be obtained by the action of an excess of water on 22 g. of calcium phosphide?
10. How many g. of phosphorus can be made by the electrothermal process from a ton of calcium phosphate (70 per cent pure)?
11. What is the molecular formula of arsenic if a liter of its vapor, recalculated to standard conditions, weighs 13.7 g.?
12. What is the leading demand for arsenic?
13. Calculate the percentage of P_2O_5 in "superphosphate," $\text{Ca}(\text{H}_2\text{PO}_4)_2$.
14. Explain the Marsh test for arsenic.

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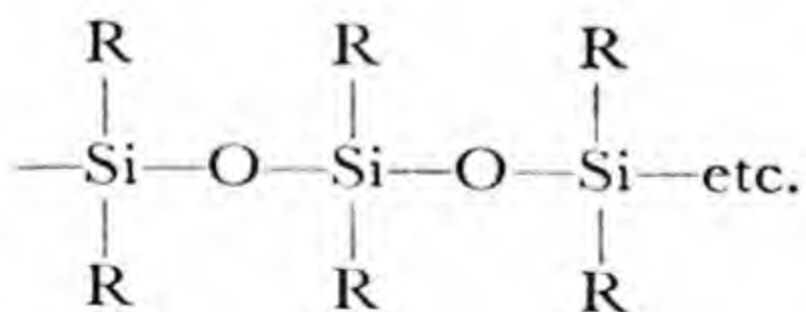
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Chapter 34 SILICON AND BORON. GLASS

SILICON

Silicon resembles carbon in its valence of four and in the weakly acid properties of its hydroxide. It also forms a series of compounds remarkably unlike the compounds of carbon, except in formulas. For example, SiH_4 is comparable to CH_4 ; SiCl_4 to CCl_4 ; and SiHCl_3 (silico-chloroform) to CHCl_3 (chloroform). There are many more such compounds of silicon, but they differ from carbon compounds in that silicon atoms will not link up with each other in large molecules as do carbon atoms.

Silicones. Although silicon atoms do not link together in long chains like carbon atoms they do form chains with alternate oxygen links.



Organic radicals are represented above by R. We have just begun to develop an intricate chemistry of these silicones, with great variations in sight. Airplane lubricating oils of this type remain fluid at 400°F above and 50°F below zero. High heat resistance of silicone varnishes makes possible far greater power in very small electric motors. Silicone rubber gaskets are used in turbo-superchargers for planes and another silicone as hydraulic fluid. An extremely durable silicone paint for automobiles is being developed.

Silane, SiH_4 , is analogous to methane, while $\text{H}_3\text{Si} \cdot \text{SiH}_3$ or Si_2H_6 , is analogous to ethane, C_2H_6 .

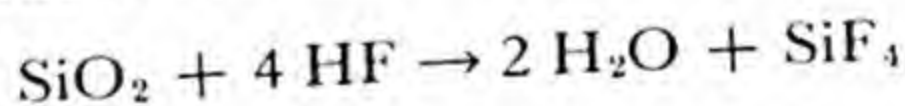
Occurrence. Silicon does not occur free but it is the commonest element after oxygen. Over one-fourth of the earth's crust is combined silicon. Its oxide (SiO_2) is found everywhere as quartz or in sand and sandstone. Clay and all common rocks except limestone and dolomite are silicates. Silicon is the central element in the mineral world much as carbon is in the plant and animal realm.

Preparation. When the dioxide is reduced with carbon in the electric furnace, ferrosilicon is produced. It is much used in steel-making to remove air bubbles.

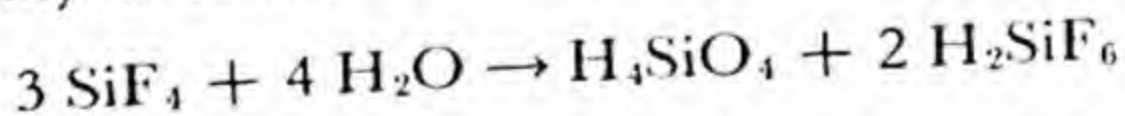
Silicon steel, containing only a few per cent of silicon, has for the past twenty-five years been used for transformer cores and in that time has saved the electrical industry hundreds of millions of dollars by decreasing the heat loss when the magnetic state of the transformer is changed. "Duriron," containing 16 per cent silicon, resists attack by hot nitric acid.

Properties. Silicon is readily attacked by the halogens, forming gaseous silicon halides. At high temperatures it forms silicides like CSi or "carborundum." Its density is 2.4 g./ml. and it melts at 1420° .

Silicon Tetrafluoride, SiF_4 . This colorless gas, formed by the attack of hydrofluoric acid on quartz, or on silicates in general



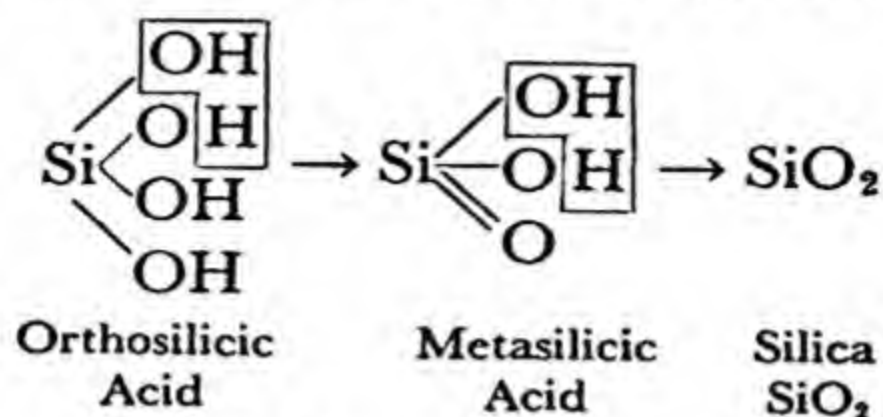
reacts vigorously with water to form a soluble complex compound, fluosilicic acid, H_2SiF_6 . The silicic acid formed at the same time may be removed by filtration:



Silicon tetrachloride, a colorless liquid, also reacts readily with water.

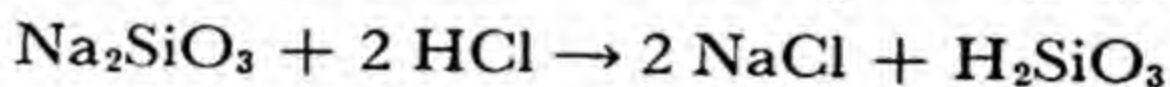
The Silicic Acids. Orthosilicic acid is prepared by hydrolysis of the chloride or decomposition of silicates with acids. It is such an extremely weak acid that its ammonium salt has never been isolated, due to its complete hydrolysis. By progressive dehydra-

tion orthosilicic acid is finally converted into its anhydride, silica (SiO_2). The loss of water is facilitated by heating:



Ethyl silicate, $\text{Si}(\text{OC}_2\text{H}_5)_4$, is hydrolized to yield silicic acid and alcohol.

A convenient laboratory method of preparing silicic acid is to acidify a soluble silicate such as "water glass" (Na_2SiO_3):



A water glass solution of 1.16 sp. gr. is added to an equal volume of approximately 8 per cent hydrochloric acid. With proper precautions the entire mass turns into solid jelly, more water being held by the silica than is called for by the formula. This jelly may be washed, and then dried in the oven to a fine powder (SiO_2). In the chapter on colloid chemistry there is more about silicic acid.

Silica, SiO_2 . Quartz or silica is one of the common minerals. It crystallizes in six-sided prisms as rock crystal.



Fig. 123. Natural quartz crystals. (Courtesy A. E. Miller.)

Above 875° quartz is slowly converted into rhombic crystals with a density of 2.2, while below that temperature the hexagonal crystals with a density of 2.0 g./ml. are stable. One form of silicon

dioxide melts at 1756° , but it is difficult to observe any sharp melting point. It softens gradually, due to its great viscosity even when fluid.

The lattice unit is SiO_4^{4-} in all crystalline silicates and in quartz crystal. This is a tetrahedron with four oxygen atoms at the corners and a silicon atom in the center.

Quartz Crystals in Radio and Radar. As a result of the observation that pressure on crystals sets up small currents of electricity, it was learned that electric stimuli could in turn cause a



Fig. 124. Heat waves and light waves are transmitted readily inside a quartz rod, even around a curve. The cigarette is ignited at the end of a cool rod. (Courtesy General Electric Company.)

crystal to expand and contract. Thin wafers sawed from perfect quartz crystals have the best "heart beats" under such stimuli.

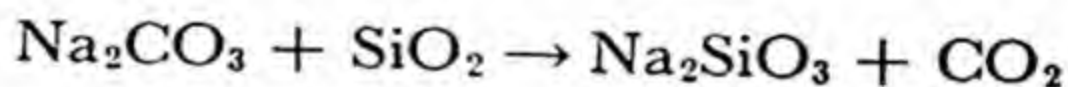
Depending on the angle of cut (relating to the optical axis), and on other factors, such wafers give sharp control over the wave frequencies sent out by broadcasting stations. Their marvelous unscrambling power makes it possible to transmit hundreds of

messages at the same time over a single telephone wire. Artillery range finders, depth-sounding instruments and "radar" in general demand quartz wafers. Brazil has been our chief source of supply of flawless crystals. The art of cutting and assembling slices developed marvelously under the stress of war. Recently crystals of ethylene diamine tartrate have replaced some of the quartz crystals.

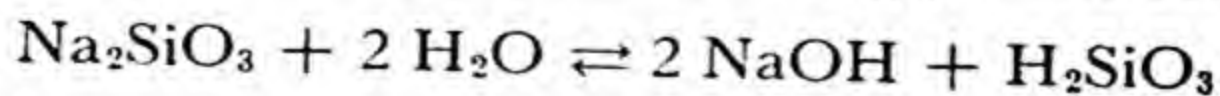
Clear Fused Quartz. Since the coefficient of expansion of quartz is only 6 per cent of that of ordinary glass it can stand sudden changes of temperature without cracking. Its small increase in length with large change of temperature makes it suitable for clock pendulums, tuning forks, and thermometers, as well as for huge lenses and reflectors in astronomical instruments. Quartz is the best solid material for transmission of ultra-violet light.

The new "Vycor" glass, 96 per cent silica, softening only above 1000°C ., is made by treating a special glass with hot acid to remove basic oxides as soluble salts, and heating the porous product to form a clear solid.

Water Glass. As the anhydride of an acid, silica reacts with bases but not with acids (except hydrofluoric acid). With fused sodium carbonate it displaces carbon dioxide, as would any ordinary acid. The volatility of one of the products, carbon dioxide, prevents reversal of the reaction:



Water glass is made by heating an excess of quartz sand with fused sodium carbonate, the proportions being determined by the various uses. Water glass is sold in great quantities (450,000 tons annually) in the form of a concentrated solution, a thick syrup of about 1.38 specific gravity. When allowed to dry it forms a brittle, glassy solid. As a salt of a weak acid and a strong base (see Hydrolysis) its aqueous solution has a strongly basic reaction:



The composition of water glass may be varied from $\text{Na}_2\text{SiO}_3 \cdot \text{SiO}_2$ to $\text{Na}_2\text{SiO}_3 \cdot 3\text{SiO}_2$ with resultant variation in properties.

Water glass has a variety of uses. It is the cheapest glue known. The heavy cardboard shipping boxes of today are built up from paper sheets thus glued

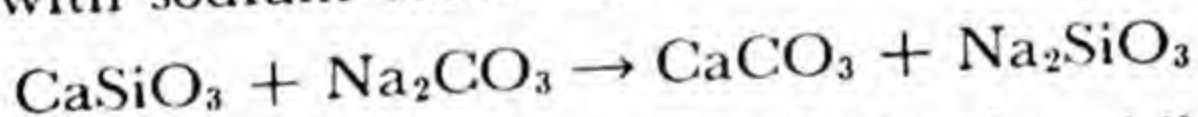
together. Artificial stone is prepared from small lumps of stone and sand, with a water-glass binder. Wood, cloth, and paper are fireproofed with water glass. It is a filler and binder in cheap soaps, and a hardener of concrete.

Sodium metasilicate, $\text{Na}_2\text{SiO}_3 \cdot 5 \text{H}_2\text{O}$, is sold in the convenient form of a soluble powder.

Silicate Minerals. Although it is difficult if not impossible to isolate definite silicic acids, salts of several different ones are found as minerals:

Orthosilicates (from H_4SiO_4)	$\left\{ \begin{array}{l} \text{Mica, } \text{KH}_2\text{Al}_3(\text{SiO}_4)_3 \\ \text{Kaolin, } \text{H}_2\text{Al}_2(\text{SiO}_4)_2 \cdot \text{H}_2\text{O} \\ \text{Garnet, } \text{Ca}_3\text{Al}_2(\text{SiO}_4)_3 \end{array} \right.$
Metasilicates (from H_2SiO_3)	$\left\{ \begin{array}{l} \text{Asbestos, } \text{CaMg}_3(\text{SiO}_3)_4 \\ \text{Soapstone or talc, } \text{Mg}_3\text{H}_2(\text{SiO}_4)_3 \\ \text{Beryl, } \text{Be}_3\text{Al}_2(\text{SiO}_3)_6 \end{array} \right.$
Disilicates (from $\text{H}_6\text{Si}_2\text{O}_7$)	Serpentine, $\text{Mg}_3\text{Si}_2\text{O}_7 \cdot 2 \text{H}_2\text{O}$
Trisilicates (from $\text{H}_4\text{Si}_3\text{O}_8$)	Orthoclase, KAlSi_3O_8

In decomposing these silicates for analysis they are powdered and fused with sodium carbonate:



The silicates dissolve in an excess of melted soda, while most carbonates do not, so the reaction is not reversible. On addition of hydrochloric acid the carbonates are converted into chlorides. Evaporation of the washed residue dehydrates the silicic acid liberated from sodium silicate. This is finally weighed as pure silica. The soluble chloride of calcium (or other metal) is removed and determined by the usual methods.

In silicate minerals a tetrahedron of oxygen atoms with a silicon atom in the center is one of the units in the crystalline lattice. Planes of these —SiO_4 units, with cations in between, are present in mica and permit its easy splitting. The Si—O—Si links in common silicates is reminiscent of the silicones.

Silicosis, a disease of the lungs caused by the industrial hazard of working in silicate dusts, has been greatly ameliorated by ten-minute breathing of air containing fine aluminum dust which probably coats the silicate particles and prevents reaction with moisture in the lungs.

Exercises

1. Write the equations representing the action of hydrochloric acid on the fusion product just discussed.
2. How many grams of water glass can be made from 150 g. of pure sand? If fused with soda, how many liters of carbon dioxide would be released?

GLASS

Glass is a mixture of silicates, usually those of sodium and calcium, although many variations are possible. Common glass might be considered as $\text{Na}_2\text{SiO}_3 \cdot \text{CaSiO}_3$, but in practice contains more silica. (Compare with water glass.) Window glass is usually $\text{Na}_2\text{O} \cdot \text{CaO} \cdot 6 \text{SiO}_2$. This does not mean that Na_2O is actually present as such. The formula is merely a convenient representation of an analysis.

In general all glasses consist of a structure in which a small positive atom, such as that of silicon, has coordinated with it four or more anions to give a lattice which has positive ions located in the interstices of the lattice. The lattice formed in a glass structure is a completely random arrangement, and on cooling no crystallization occurs. The positive ions usually are not fixed in the lattice, can be replaced in the structure by leaching processes, and can be made to move slightly in an electric field. By considering the ionic radii, valence numbers and the bond strengths in such structures, one can predict to some extent which combination of elements will form glasses.

In the silica glasses the lattice is composed of SiO_4 tetrahedrals with positive ions, Na, Ca, Pb, Al, etc., in the interstices of the structure. In phosphate glasses a similar tetrahedral ion, PO_4^{3-} is the basis for the lattice. When in combination with aluminum oxide no alkali metal ions are required and a very satisfactory product is obtained. Phosphate glasses containing iron have a wide absorption band in the infra-red and are used as heat absorbing filters. Phosphate glasses are somewhat more water soluble than silicates, but are quite resistant to HF. Beryllium-lithium borate glass is very transparent to X-rays.

Glass making was one of the earliest arts. Glass beads were found in the tombs of the rulers of the First Egyptian Dynasty

(5000 B.C.) and glass tear bottles were discovered in the tombs of later Pharaohs (about 4700 B.C.).

Transparent glass came later — during the Hellenic era — and was under suspicion of being the product of black magic.

When the Romans conquered Egypt about 23 B.C., they gladly took tribute in glass and carried glass-makers to Rome.

In glass making silicon dioxide, a non-volatile acid anhydride, drives out the volatile carbon dioxide from carbonates of calcium and sodium.

Common Glass. Glass is made by melting sand, lime, and soda in a gas-heated furnace. If iron is present as an impurity, the glass is green. This is the color of ferrous silicate. Since ferric silicate has a very weak yellow color it is an advantage to oxidize the green ferrous salt with manganese dioxide. Too much manganese introduces the amethyst of manganese silicate. Selenium is now replacing manganese dioxide as a color corrector. Soft, or low-melting, glass is of the lime-soda type. Hard glass, of higher melting point, is prepared by substituting potassium carbonate for the sodium carbonate. Until recently red glasses were made by addition of gold, cadmium sulfoselenide, copper, or antimony sulfide but now a red uranium glass is available.

Cheaper and purer sodium carbonate produced by the Solvay Process revolutionized glass making.

Window glass was once made by blowing a ball into a cylinder, which was cut open while hot, and allowed to flatten in the annealing oven. Bottles are made by blowing the glass in a mold. Where window-glass cylinders were formerly blown by the lung power of strong men, they are now blown by machines. A hollow ring is lowered into a batch of molten glass, a bubble started and then the ring is raised while air is blown into the bubble. As a result a beautiful glowing cylinder forty feet high and two feet wide is suspended in the dark factory like a pillar of light. This cylinder is lowered to supports, cut open, allowed to flatten and in general handled like the old six-foot cylinders.

Flat glass (plate or window) now is made by being drawn from a molten batch by an iron bar three inches wide and six feet long.

This bar is attached to flexible metal strips so the slowly moving sheet can be run over bending rolls to the flattening table. It is finally cut into sheets and acid-cleaned.

The Owens bottle-blowing machine now does the work of fifty men; a single machine makes 10,000 bottles per hour. This rate of production is evidently needed, for the United States uses four billion bottles yearly.

Plate glass is cast on a wide iron table, rolled flat, and, when cold, ground to remove unevenness and polished with rouge. In some factories the plate glass melt is allowed to flow on to a revolving drum and is then passed under a roller, cut into sheets, and annealed.

The automobile industry has created a demand for plate glass exceeding even that of show windows. The possibility of accident and injury from flying glass has led to the use of non-shattering glass windshields and windows. Two layers of sheet glass and a middle layer of transparent butyral plastic with a suitable adhesive are powerfully compressed. Under impact the flexible center layer holds broken fragments. A similar laminated glass (five layers) is in use for bullet-proof windows in bank offices. Such a glass one inch thick turns aside machine gun fire at 45 feet.

Tempered glass, a recent product, is important because it is five times stronger than plate, more flexible, better able to stand sudden temperature changes, and crumbles but does not splinter when broken. Sudden cooling (by air) of the surface gives this glass its toughness.

Optical Glass. Glass for lenses and cut glass must have a high index of refraction and this property is obtained by substitution of oxides of lead, barium, zinc, cadmium, or magnesium for all or part of the calcium oxide. Oxides of boron or titanium may also replace all or part of the silica. Rare earth oxides may be used to give low optical dispersive power.

Resistance glass of the pyrex type contains some boron trioxide in place of part of the silica. It resists the attack of chemical reagents very well and is essential to the laboratory. Since it expands very little with heating, it is not likely to crack with sudden temperature changes. This property, with its unusual strength, made pyrex glass very popular for baking dishes.

Glass textiles have recently come into use wholly because the filaments are now drawn much smaller than ever before with a

resultant great increase in strength. Fibers have been made 30 miles long without a break.

The average diameter of a single filament is 0.00025 inch, but they can be drawn to 0.00005 inch. (Human hair averages 0.001 inch.) A single filament has a tensile strength of 1,500,000 pounds per square inch cross-section, but a 60-strand thread has a strength of only 17,000 pounds. Two pounds of the finest filament would encircle the earth.

A large market immediately developed for glass fibers woven into electric insulating tape, and another market for fluffy blanket heat insulation of houses, ships, and locomotives, and still another for dust removal from conditioned air. Durable window hangings and theater curtains are possible, but glass clothes would slightly irritate the skin. These strong fibers can reinforce plastics. On one battleship 30 tons of weight were saved by substituting glass blankets for heavier heat insulation. Broken down glass fibers have been incorporated in sound-deadening paints to be sprayed on metal. Bullet-proof jackets for some of our military forces were made of fine glass filament fabric laminated with a plastic. They could stop a .45-caliber pistol bullet.

Glass bricks and hollow tile, tinted and translucent, are now available for architectural purposes, tempting us to dream of softly luminous buildings. Light foam glass also has its uses.

How we should live without glass is difficult to imagine. All factory work would depend on the weather, so that costs would rise. Houses would be poorly lighted by day and without our lamp chimneys or our 900 million electric light bulbs per year (in America) there would be very little study or other reading by night.

Bottles for milk, medicine, and drinks would be lacking. We should know little of the stars and less of bacteria, and defective eyesight would go uncorrected. Photography and the motion picture would be unknown. Perhaps lenses of plastics might be used to a limited extent.

When Leeuwenhoek in 1675 contrived a crude microscope and saw bacteria and protozoa in water ("wee beasties") he gave the world knowledge of greater importance than the rise and fall of

empires — yet the world yawned and disregarded his discoveries for nearly two centuries.

Films of metallic fluorides, one-fourth the wave length of light, deposited by vacuum evaporation on glass lenses, cut down the 4 to 6 per cent loss of light by reflection at each air-glass surface. The advantage in optical instruments, cameras and movie projectors is obvious.

Enamels are glasses somewhat varied in composition. They are made white by suspended tin oxide or calcium phosphate or fluorspar. They may contain much Al_2O_3 , and B_2O_3 and Sb_2O_3 as well as SiO_2 .

3. How could you make a blue enamel?

BORON

Boron, with a valence number of three, belongs with the aluminum family and not with tetravalent carbon and silicon. It is a more pronounced acid former than aluminum and in chemical properties is much nearer silicon. Its density is 2.45 g./ml. and it melts at 2300° .

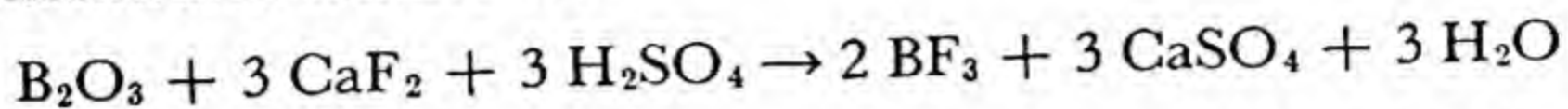
Boron, prepared by reduction of its oxide with magnesium, has the interesting property of uniting, when hot, with both oxygen and nitrogen, but it has, as yet, no great commercial use as the free element. Boron is hard enough to scratch rubies.

Boron has also been prepared as a secondary product of the electrolysis of fused oxide and a borate. The free element reacts rapidly with chlorine and bromine above 400° . It is also readily oxidized to boric acid by nitric acid.

Boron carbide, B_4C , a new product of the electric furnace, is next to the diamond in hardness. Boric acid is reduced at high temperature by pure coke and simultaneously the boron released unites with carbon.

Its extreme resistance to abrasion makes boron carbide suitable for sand-blast nozzles, wire-drawing dies, and jeweled bearings. In powdered form it can be compressed in molds, electrically fused, and molded to desired shapes.

Boron Trifluoride, BF_3 . Boron trifluoride is a gas, and is evolved when boron trioxide is heated with calcium fluoride and concentrated sulfuric acid:



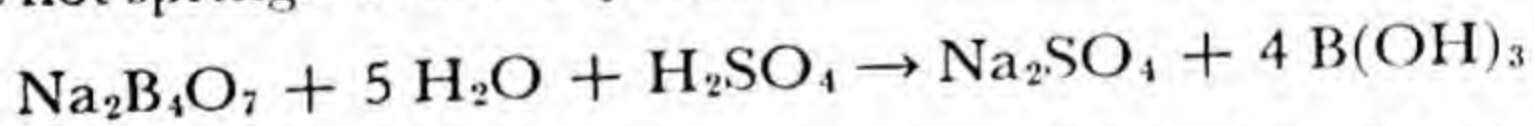
It is now much used as a catalyst in many organic reactions, especially where water is a product. It may take up the water by coördination or by hydrolysis.

The metal fluoborates are used in electroplating with lead, tin, zinc, copper, and cadmium. Copper fluoborate is $\text{Cu}(\text{BF}_4)_2$.

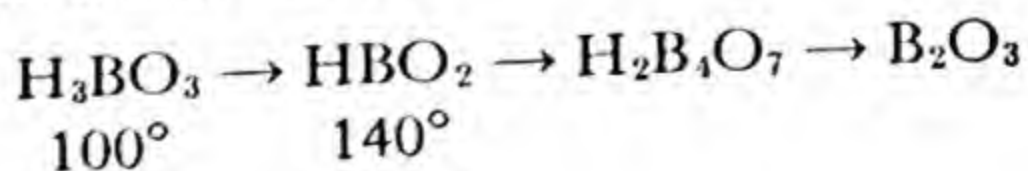
Boron nitride, one of the hardest substances known, can be prepared by fusing together borax and ammonium chloride.

Occurrence. On cooling the water from certain hot springs in Italy, boric acid, $\text{B}(\text{OH})_3$, deposits as greasy, white crystals. Borax, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10 \text{H}_2\text{O}$, is found in Death Valley, California. Boracite, a complex magnesium salt, is found in the Stassfurt mines. Colemanite, $\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 5 \text{H}_2\text{O}$, and rasorite or kernite, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 4 \text{H}_2\text{O}$, are plentiful in California, a state that has almost a monopoly on boron compounds. The United States produced 360,000 tons of borates in a recent year, ninety per cent of the world's output.

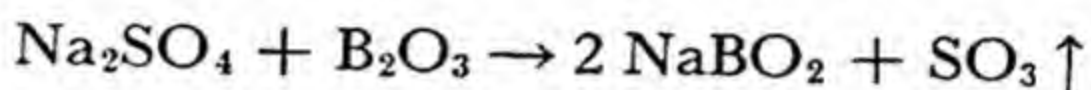
Boric Acid, H_3BO_3 . Boric acid, as was mentioned, occurs in some hot springs. It is also prepared by acidifying borax solutions.



Boric acid in solution is very faintly acid and so its use as a mildly antiseptic eyewash is not complicated by hydrogen ions. Purification of this acid is easy because it is volatile with steam. Identification is also easy since it imparts a green color to a gas flame. On being heated to 100° it changes by partial dehydration to metaboric acid, at 140° to tetraboric acid, and at high temperatures to the anhydride. Boron trioxide is a hygroscopic glassy solid melting at about 1300° :

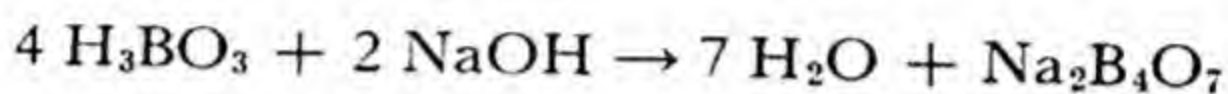


The non-volatile acidic anhydrides such as SiO_2 and B_2O_3 are very useful at high temperatures. For example:



This reaction seems strange, for H_2SO_4 is a stronger acid than H_3BO_3 , but the reaction proceeds effectively because SO_3 is volatile and B_2O_3 is not.

Borax, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10 \text{H}_2\text{O}$. Borax can be made by the addition of sodium hydroxide or carbonate to boric acid, although this is not the method commonly used:

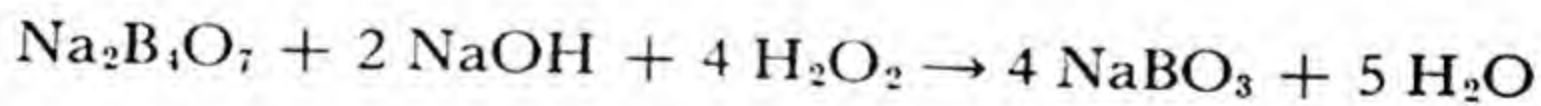


Since borax precipitates Ca^{++} and Mg^{++} ions from hard water and its solution is strongly basic (by hydrolysis) it is useful in softening water and in cleansing. As a flux in soldering it has another use. The formula might well be written as $2 \text{NaBO}_2 \cdot \text{B}_2\text{O}_3$, which shows that borax is really sodium metaborate with the acid anhydride. When melted between hot metal plates, as in welding or soldering, this acid anhydride reacts with metallic oxides (rust) to form easily fusible slags which are squeezed out, leaving clean metal surfaces for good contact. Borax beads used in the analysis of metallic compounds may form, when heated, metaborates of characteristic colors (blue with cobalt, etc.). Borax is used in glass, soaps, pottery, and enamels, in canning, as a preservative, and as an antiseptic. Half of the total amount consumed goes into pottery and enamels.

Borax solutions turn turmeric paper brown. Acidified borax colors a gas flame both yellow (due to the sodium) and green (due to the liberated boric acid).

Borax is used for snow on indoor ski slides.

Sodium Perborate, $\text{NaBO}_3 \cdot 4 \text{H}_2\text{O}$. Borax reacts with cold sodium hydroxide and an excess of hydrogen peroxide to form a perborate.



It is a valuable bleaching agent, antiseptic, and bactericide, due to its easy hydrolysis in water with release of hydrogen peroxide.

The formula may be written, $\text{Na}-\text{O}-\text{O}-\text{B}=\text{O}$, sometimes called sodium peroxyborate.

In one commercial process sodium perborate is prepared by electrolysis of a mixture of borax and sodium carbonate equivalent to sodium metaborate, NaBO_2 , $4 \text{H}_2\text{O}$. The hydrogen peroxide formed by electrolysis of this solution reacts with sodium borate to form the perborate, NaBO_3 .

Exercises

4. Hot boron unites with nitrogen to form a white solid. What must be the formula and name? What similar compounds have been studied?
5. Why is silicon so tremendously important in compounds? Has the free element any uses?
6. Calculate the percentage composition of orthoclase (KAlSi_3O_8).
7. What weight of water of hydration can be obtained from 617 kg. of borax? What is the percentage of water in the crystal?
8. What type of glass is used in baking dishes?
9. For what uses is quartz superior to glass?
10. Why are glass fabrics useful?
11. How much sodium silicate can be made from 800 kg. of sand (90 per cent pure quartz)?
12. How is "non-shattering glass" manufactured?
13. Is silicon the central element in all glasses?

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Chapter 35 COLLOID CHEMISTRY

Strictly speaking, there are no such things as *colloids*, for most, if not all, substances can be prepared in the "colloidal state." However, the term *colloid* is too convenient to drop.

"Colloid chemistry," writes Bancroft, "is the chemistry of grains, drops, bubbles, filaments, and films." By grains we mean small solid particles. Drops are small liquid particles, and bubbles small gas particles. In filaments, all dimensions but one are very small, while in films only one dimension is small. These particles must be surrounded by, or dispersed in, some other substance or another form of the same substance. "Colloidal dispersion" is a useful phrase.

But after all we are interested colloiddally in grains, drops, filaments, and films only when they are sufficiently small, of diameters ranging from about 200 $m\mu$ to 1 $m\mu$. (A millimicron, 1 $m\mu$, is one millionth of a millimeter.) The smallest particle resolvable with the aid of the best microscope is about 100 $m\mu$ in diameter, while the largest molecules approach a diameter of 1 $m\mu$. Most colloidal particles are aggregates of hundreds or thousands of molecules. When colloidal units or aggregates coalesce into still larger aggregates they may be precipitated from suspension. Unless such coagulated material becomes distinctly crystalline on standing, we are in the habit of calling it colloidal, as in the case of cheese, for example.

Grains	{	Dispersed in another solid	{ Gold in ruby glass Sodium in blue rock salt Elements or compounds in some alloys
		Dispersed in a liquid	{ Colloidal gold in water Colloidal selenium in water
		Dispersed in a gas	{ Dust Visible smoke
Drops	{	Dispersed in a solid	{ Water in butter
		Dispersed in a liquid	{ Oil-in-water emulsions (milk)
		Dispersed in a gas	{ Mist Fog
Bubbles	{	Dispersed in a solid	{ Air in meerschaum Air in pumice stone
		Dispersed in a liquid	{ Foam
		Dispersed in a gas	{ Impossible because gases form molecular mixtures
Filaments	{	Any solid fibrous material may contain filaments of minute diameter	
Films	{	Films may be liquid or solid, but they must be very thin; soap bubble films have one colloidal dimension	

New properties of matter appear when a given substance is colloidally dispersed. The effect of gravity is counteracted somewhat, while surface tension, electric charge, and other forms of energy increase greatly. Gold, yellow in the mass, may be dispersed in water to form what is apparently a blue solution. With still finer dispersion it is red, when it is just short of molecular dispersion. The brightest red particles of colloidal gold are about $6\text{ m}\mu$ in diameter.

It may be stated with reservations that acids, bases, salts, sugars, and crystalline substances in general are molecularly dispersed in water solution, while the glues, gums, resins, starch, cellulose, rubber, and non-crystalline substances in general are colloidally dispersed in suitable solvents.

Yet this statement must be qualified, for in alcohol the common soaps are molecularly dispersed in true solution, while in cold water they are colloidally dispersed, each particle being composed of many molecules, ions, and water.

The dye called Congo rubin in true solution in water is red while the portion precipitated by salts, and settling very slowly, is blue. Mixtures of the two colors are violet. Warming the blue solution turns it red but on cooling the blue colloidal form reappears.

Many substances previously called amorphous (non-crystalline) and colloidal have recently shown an ultramicrocrystalline structure under the searching eye of the X-ray. However, this makes no difference in our definition, for the colloid conception is now solely that of size of particle.

Why Colloidal Particles Remain in Suspension. Gold is much heavier than water, yet red gold-suspensions-in-water have been kept for many years without settling. There are at least three good reasons for the stability of ordinary colloid suspensions. These are the Brownian movement, the presence of electric charges on particles and of protecting films around them.

1. Brownian Movement. Water molecules, always in constant motion when above absolute zero, bombard the suspended particles of colloidal gold from all sides. The gold particles are

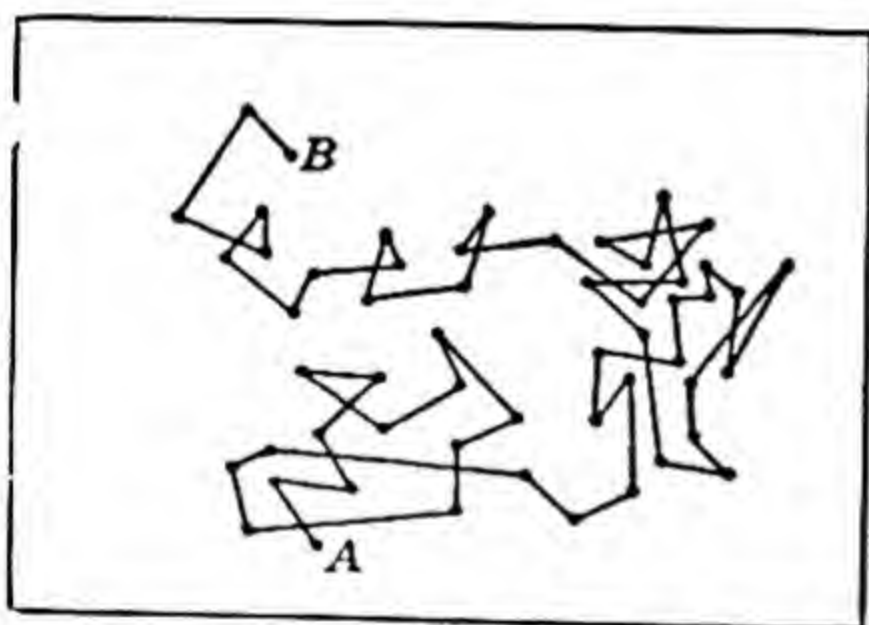


Fig. 125. Brownian movement.

moved some distance, of course, but when such particles are large enough to be visible to the unaided eye, this motion is too slight to be of much help and the gold settles rapidly. But gold aggregates under $100\text{ m}\mu$ in diameter are projected appreciable distances by the water molecules. This vigorous stirring effect is perpetual. Under

the lens of the ultra-microscope this Brownian movement is startling. The gold particles dart with zigzag motion in all directions (Fig. 125). At this point the observing student remembers that colloidal gold particles are not visible under the microscope. How, then, is this motion apparent? The suspension is examined in a dark field while a strong beam of light entering at right angles to the line of vision makes the gold particles visible as mere points of light without apparent diameter. This

Brownian movement furnishes convincing proof of the reality of molecules, for it is the molecules that do the bombarding.

The suspended colloid particles must have kinetic energy of their own just as truly as have the molecules, but, being heavier, their actual motion is less.

2. Electric Charge. Most colloid particles in suspension move slowly in an electrolytic cell as if attracted by the charged poles, and they are coagulated into coarse aggregates on contact with the attracting poles. This means that the particles are electrically charged bodies. In some suspensions, such as arsenic sulfide, all the particles are attracted to the anode, hence are negatively charged. Ferric hydroxide particles are all positive. Particles bearing like charges, free to move, must repel each other, thus tending to remain scattered or suspended throughout the liquid.

3. Protecting Films. A film of gelatin or of any one of various gummy substances can surround each suspended particle so that the particles have difficulty in touching. Under such conditions coalescence into aggregates too large for help from the Brownian movement is difficult. Any influence tending to keep the aggregates small aids stability.

Methods of Preparation. Reaction between dissolved substances may yield precipitates or may yield colloidal aggregates. In the latter case colloidal suspensions are formed by *condensation* of smaller particles into larger ones.

Dispersion methods are the exact opposite of condensation methods: larger particles are broken down into smaller.

Dispersion Methods.

1. Mechanical Disintegrations. The simplest method in principle, but not always suitable in practice, is fine grinding. Most of the modern "colloid mills" have two parts rotating (high speed) with very small clearance. Solid particles in a wet slurry are disintegrated — but not so finely as to give particles of 1 to 200 $m\mu$ dimensions. Consequently these "colloid mills," although useful, are wrongly named.

2. Peptization by Liquids. By peptization we mean disintegration into colloidal particles through the action of some added chemical. Water has long been used as a peptizing agent in *dis-*

solving glue, gelatin, agar, and such substances. In reality, the glue or gelatin is not dissolved in the true sense of molecular dispersion, but is only colloiddally dispersed. Hot water has a more rapid peptizing action than cold. Acetone is said to dissolve pyroxylin but it only peptizes the solid.

3. Peptization with Ions. Colloid particles have an ability to hold to their surfaces (to adsorb) other substances, even ions. A given surface may have a preference for certain ions and thus in one case acquire a positive charge by holding a positive ion, charge and all, while another kind of colloid may choose to acquire a negative ion and charge. This reminds us of one of the reasons for stability — like charges on the particles with consequent repelling or stirring action. It is thus evident that a colloid may be stabilized, kept in suspension, by adsorption of ions.

Silver bromide formed in the presence of a slight excess of Ag^+ ions fails to precipitate. The adsorbed Ag^+ ions give their positive charge to the silver bromide particles, thus suspending them. With a slight excess of Br^- ions the suspension is negatively charged, due to preferential adsorption of negative Br^- ions.

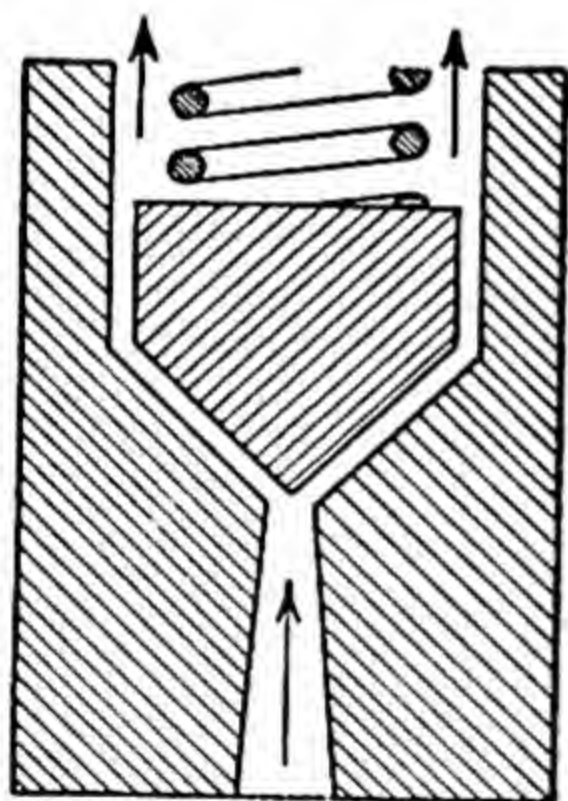


Fig. 126. Homogenizer for reducing the size of droplets in emulsions. The spring is set so that the needle valve is forced open when liquid enters at a pressure of 2000 pounds.

The enormous ceramic industry deals largely with the colloidal nature of clays. To mention a single point, wet clays to be poured into molds for making heavy porcelain objects must carry a good deal of water. But in drying and baking this wet clay there is great shrinkage and distortion. Obviously if the desired fluidity could be secured with less water there would be less warping. A very little sodium hydroxide makes this possible. Adsorption of hydroxide ions peptizes the clay so that it flows as well into molds as if it contained much more water.

4. Emulsification. One liquid may be dispersed in a second (if they are immiscible) by mere shaking or stirring, but such

dispersions, or *emulsions*, are temporary, quickly separating into their components. To make emulsions is easy; to keep them is difficult.

Shake water and kerosene together. On standing, the high surface tension of the water drops pulls them into one big drop or layer because of the tendency to expose the least possible surface. By lowering this surface tension of water the emulsion should keep longer. Shake kerosene with a 1 per cent aqueous solution of sodium oleate (a soap which greatly lowers the surface tension of water). A thick, creamy emulsion of drops of oil dispersed in water results and keeps fairly well. As in the case of milk, an emulsion of fat globules in water, etc., a cream slowly separates. This is merely a layer of a richer emulsion above a poorer one.

Now add any acid to this emulsion. It breaks because the added acid destroys the soap, the emulsifying agent. Other emulsifying agents than soaps are possible. Gelatin, 0.4 per cent, can be used for kerosene-in-water. Gum arabic is useful and, with the proper liquids, cellulose nitrate will serve. Mayonnaise is an emulsion of olive oil in water (or vinegar), with the colloidal protein of the egg as emulsifying agent.

By slowly adding an oil to soapy water with vigorous agitation, Pickering made an emulsion of 99 per cent oil (as separate drops) and 1 per cent water (films between the drops). This emulsion when cut into a cube retained its shape.

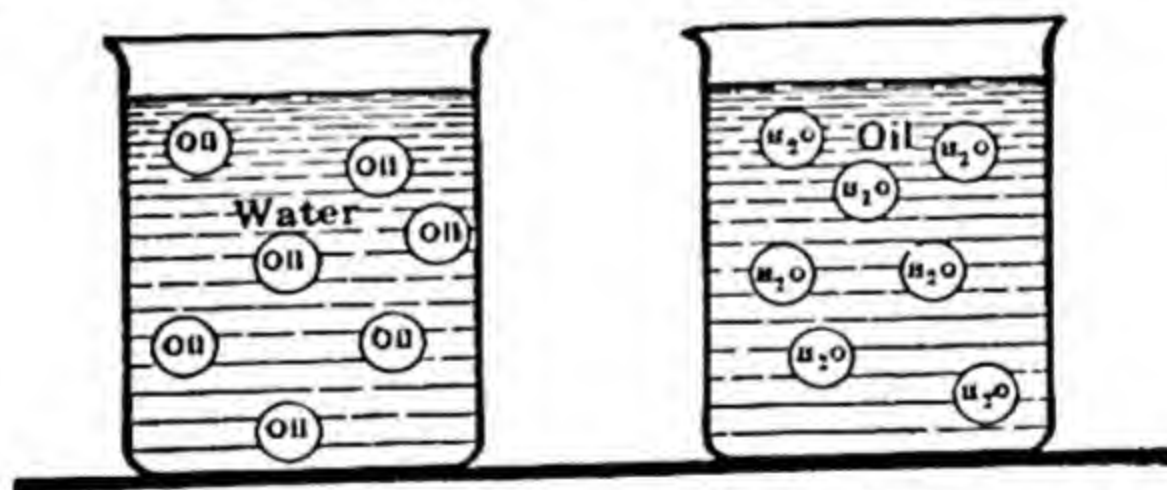


Fig. 127. Two types of emulsions.

Surface tension lowering as by soap in water often exerts considerable influence in emulsification. Concentration of the emulsifying agent into adsorption films around the drops is usually the leading factor in preventing coalescence.

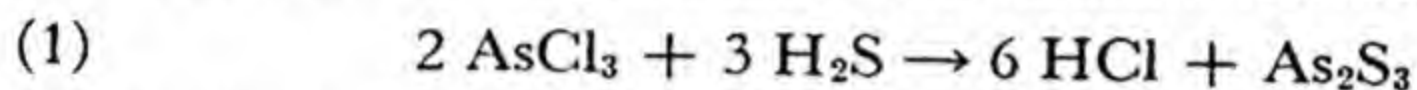
Oil-in-water emulsions result when the emulsifying agent is dispersed in the water, but water-in-oil emulsions are formed when the agent is dispersed in the oil. Emulsion paints, fast drying, are now largely used for interior work.

Condensation Methods.

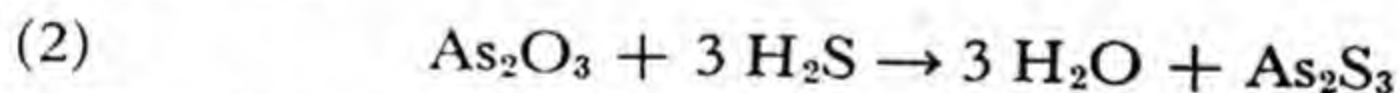
5. Reduction. Salts of gold, silver, mercury, platinum, and palladium in water are easily reduced to the free metal. Under favorable conditions beautiful suspensions form. Very dilute gold chloride solutions made neutral by a trace of potassium carbonate are reduced very easily.

Mix 2 ml. of 1 per cent gold chloride solution with 98 ml. of water. Dissolve 0.5 g. tannin in 100 ml. water. Heat both solutions and mix equal parts, adding one to the other rather slowly. A clear red or blue suspension results.

6. Formation in Low Ion Concentration. A familiar reaction is that between hydrogen sulfide and arsenic trichloride:



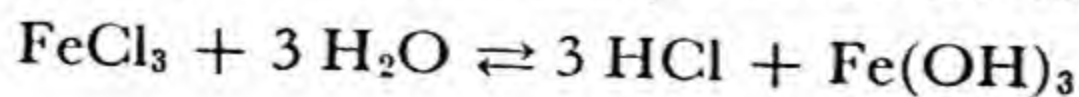
The yellow sulfide settles out quickly. Yet if some arsenious oxide is boiled in water and the solution filtered, any addition of hydrogen sulfide fails to yield a precipitate. A lemon-yellow suspension is obtained:



The essential difference between (1) and (2) is that in (1) the by-product is an acid which ionizes, while in (2) the by-product is only water. Addition of a little hydrochloric acid or even some salt to the yellow colloid suspension coagulates the sulfide, with consequent quick settling. The suspended particles are negatively charged, and it is obvious that this charge could be neutralized by positive ions, such as hydrogen, sodium, and others. Loss of charge means less ability to remain suspended.

To secure a suspension of any insoluble salt, while it is forming there is required an absence of oppositely charged ions or at least a very low concentration of such ions.

7. Hydrolysis. If into a beaker of boiling water a few ml. of 30 per cent ferric chloride are poured, a rich red colloidal suspension of ferric hydroxide forms instantly. This is a useful preparation because it is a typical positive colloid and keeps a long time. Hydroxides of aluminum and chromium may be made, but not quite so easily. Other methods are preferred for them.



Dialysis. Making colloidal dispersions is one matter, keeping them is another. Since ions of opposite charge tend to coagulate suspensions, a measure of safety should be secured by removing these ions. Fortunately there is a method for accomplishing this, namely, dialysis.

Many membranes, such as bladder, intestine, peritoneum, cellophane, parchment paper, egg skin, and the like, are permeable to water and ions but not to the larger aggregates known as colloids.

To show dialysis quickly, tie a sheet of goldbeater's skin or wet parchment paper free from pin holes around a large one-holed cork through which passes a funnel for filling purposes. In a large beaker of water suspend the parchment bag filled with cold, freshly made colloidal ferric hydroxide. This is a mixture of water, colloidal aggregates of ferric hydroxide, and the ions of hydrochloric acid. The smaller ions and molecules pass out through the membrane, and if the outer water is frequently changed they are almost completely removed, leaving only ferric hydroxide suspended in water. The last trace of ions is often difficult to remove and even may be necessary to the stability of the colloid.

In trying the experiment with colloidal ferric hydroxide, samples of the dialysate (corresponding to filtrate) should be removed in a few minutes, and tested with silver nitrate. The passage of chlorides through the membrane is very rapid.

Cellophane Sausage-Skin Dialyzers. The development of artificial sausage skins from tubular forms of viscose (cellophane) has given the colloid chemist a valuable tool. These membranes are very permeable or rapid in action and most convenient in form. The usual form is about 1 inch (2.5 cm.) in diameter but a large size (about 8 cm.) with thicker wall may be obtained. The cost is low. Purchase from the Visking Corporation, 6733 West 65th St., Chicago.

Close one end of a sausage skin by tying a tight knot with strong cord, insert a funnel of a convenient length in the other moistened end and pour in any convenient colloid sol. Tie the upper end around a glass rod, or insert a cork stopper in it and support in any way desired. Hang it in a vessel of pure water, and observe the passage of ions through the viscose membrane.

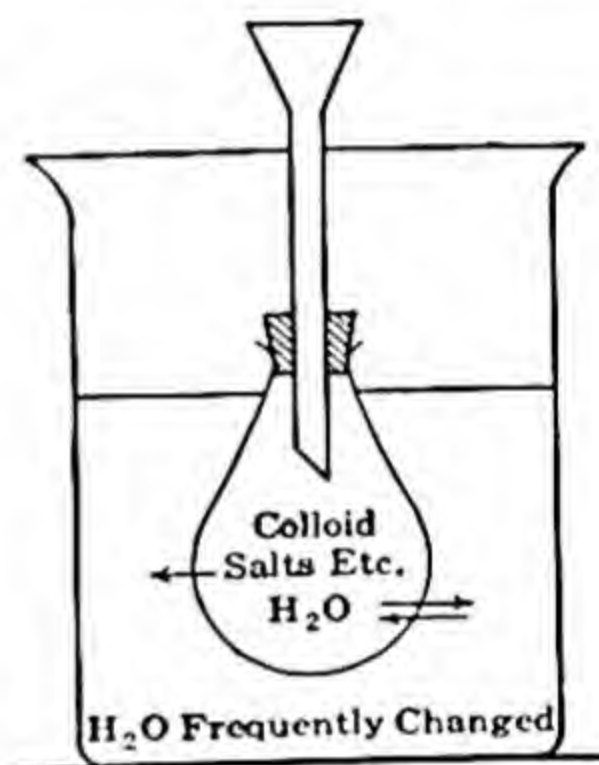


Fig. 128. Purification of a colloid suspension by dialysis through a semipermeable membrane.

Classification. *Suspensoids*, like gold, are easily coagulated by very small quantities of electrolytes and have a viscosity but little more than that of the liquid in which they are dispersed. *Emulsoids*, water suspensions of gelatin, agar, glue, starch paste, soaps, egg albumin, silicic acid, and the like, are coagulated only by relatively large quantities of salts and are extremely viscous. A 1 per cent suspension of agar in water is a solid jelly at room temperatures as is a 1 per cent suspension of sodium stearate soap.

Adsorption. A cube 1 cm. on edge has a surface of 6 sq. cm. If subdivided into smaller cubes, each only 100 m μ on edge, the total surface is 600,000 sq. cm. and there are 10^{15} particles. If further subdivided into the colloidal realm of 10 m μ on edge, the total surface becomes 6,000,000 sq. cm. In number the particles have grown from one to 10^{18} . This vast increase of surface magnifies all surface influences. Adsorption has already been mentioned as a holding of various substances to specific surfaces. The adsorptive power of a definite weight of carbon, for example, may be vastly increased by subdividing the carbon. Bone charcoal is used in sugar refineries to decolorize sugar syrup by adsorption of coloring matter. A sugar refiner buys this carbon for its surface, so size of particle means something to him.

Adsorption of toxic gases by coconut charcoal is familiar to all after the experiences of World War I. Yet the application of the principles of gas adsorption by activated carbon, silica gel, etc., is now a peace-time matter of great commercial importance. Silicic acid, formed as a gel, washed, and dried to a content of 5 per cent water, is a glassy material shot through with innumerable capillary pores of diameter not much greater than that of molecules. In these capillary pores gases are brought well within the range of molecular attractive forces, and so are held or "adsorbed."

Adsorbent carbon has certain advantages over silica gel, and, at present, has considerable industrial use.

The tenacity with which glass vessels retain a film of air when evacuated, even at elevated temperatures, shows us that a layer of gas molecules may be powerfully adsorbed by solid surfaces.

Carbon black may occupy only five per cent of its own apparent volume, the rest being adsorbed air, and air free to move between particles.

Silica gel and activated alumina dry gases by their own capillarity, condensing water vapor in their submicroscopic capillaries far more readily than they do gases such as oxygen and nitrogen.

ADSORPTION OF GASES BY ACTIVATED CARBON

(On 1 g. at 15° and Atmospheric Pressure)

	BOIL. PT.	ML. ADSORBED
SO ₂	-10°	380
NH ₃	-33.4°	181
CO ₂	-78.5°	48
O ₂	-183°	8

Remy offers this table as evidence that vapors and gases are adsorbed the more readily the nearer their boiling point to the temperature of the charcoal. If the temperature of adsorption (in this case mainly capillary condensation) were brought down within 25°, for example, of the boiling point of oxygen this gas also would be splendidly adsorbed.

Decolorizing charcoals or carbons are made from bones, coconut shells, lignite, husks, peach-nut shells, cane trash, cobs, corn stalks, peat, coals of various kinds and many other vegetable materials.

By preferential adsorption these ultra-porous carbons ("activated carbons") remove color from sugar syrup, tastes and odors from water (even an excess of chlorine), recover volatile solvents from the air of certain factories, capture gasoline from natural gas, and are generally useful.

In one experiment the complex ammonia ions of copper were so strongly adsorbed by silica gel that traces of copper could not be found in the supernatant liquid above the gel, even two years after the adsorption.

Because of the deep blue color of the Cu (NH₃)₄⁺⁺ ions and the white appearance of a column of silica gel powder a convincing lecture demonstration of adsorption is easily managed.

Adsorption may be considered a concentration of dissolved or dispersed substance upon the solid or liquid or gaseous adsorbing surface.

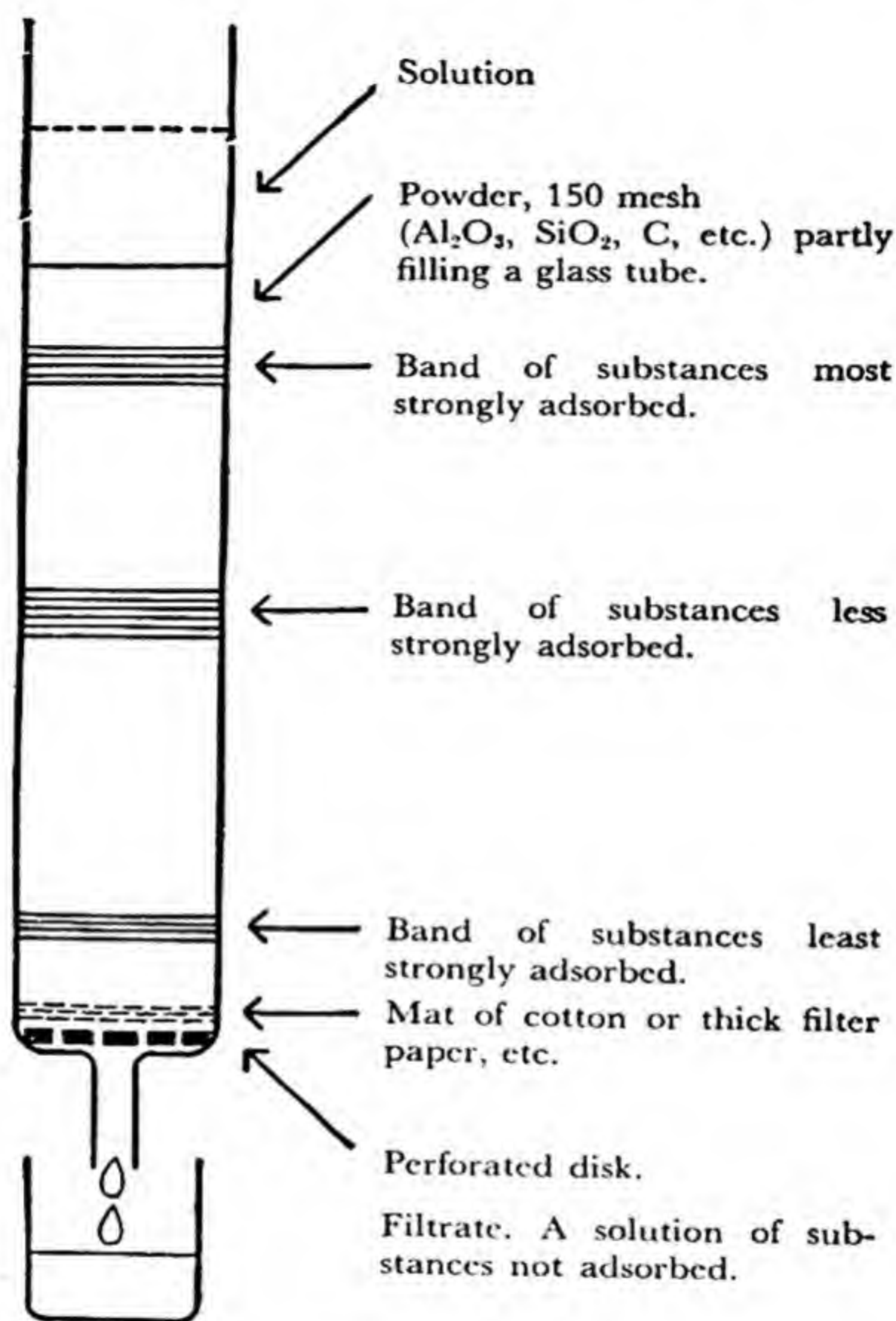


Fig. 129. Adsorption column for Chromatographic Analysis. Useful in separating and detecting substances mixed in solution. Water, benzene, petroleum, ether, alcohol, and other solvents are used. The bands, visible if colored, may be washed down and through the column by pure solvent or by a better solvent.

Soap Cleansing. The cleansing action of soap is in part an adsorption phenomenon. Soap in water is colloiddally dispersed and so exposes great surface. It has a strong adsorptive power towards dirt, and carries dirt away on the surfaces of its particles.

Furthermore the great lowering of surface tension of water and increase in wetting power caused by soap permits the soapy water to slip in between particles of dirt and fabric, etc., thus loosening dirt. The froth helps to carry off this dislodged dirt. If oil and grease are present they are emulsified on rubbing and float off as minute droplets.

Coagulation. In general the suspensoids are coagulated by the addition of oppositely charged ions. The divalent ions are far more than twice as effective in precipitating power as the monovalent ions, while the trivalent ions are hundreds of times as effective. This enables us to recognize the charge on a colloid.

Test the precipitating power of 0.05 molar solutions of NaCl , Na_2SO_4 , BaCl_2 , and AlCl_3 on such typical positive and negative colloids as ferric hydroxide and arsenic sulfide. Add the salt solutions slowly. If the divalent sulfate ion has the highest precipitating power, the colloid must be opposite in charge, namely, positive. If, on the other hand, the trivalent aluminum ion has the greatest precipitating power, the colloid must have an opposite charge, negative.

Hardy observed that a colloid was most unstable at the *isoelectric point*. This point was recognized by a failure to migrate in an electrical field (electrophoresis), showing electrical neutrality.

Smokes and mists owe much of their stability to their electrical charge and to adsorbed films of air or other gas. Hence Cottrell's high-voltage electro-precipitation method is of great use in recovery of smelter fumes and acid mists and in removal of dust from air of home or factory.

Protective Colloids. Gelatin is a protective colloid and forms a film around separate particles of silver bromide so they cannot touch each other and coalesce. These protective colloids are all organic compounds, hence the order to destroy all organic matter in qualitative analysis. Desired precipitations might easily be prevented by such organic matter.

Gels and Jellies. On cooling a hot-water suspension or solution of sodium stearate soap a translucent solid called a jelly or gel results if the soap concentration is about 1 per cent or more. A 1 per cent hot gelatin solution "sets" to a jelly on cooling, as

does a 2 per cent agar solution. There is some sort of regular structure of filaments, honeycomb or flattened coalescing spheres of highly hydrated material, in the aqueous jelly. At any rate electrolytes and many other substances diffuse through jellies with astonishing ease. The term *hydrated* applies only to water systems. Jellies made from other liquids are known and they are described by the broader term *solvated*.

The highly hydrated tissues of the body are gels. Protein is capable of swelling in water, of taking up the water, especially in the presence of a little acid or base. Accumulation of acid in the body through disease may show its effects in undue swelling (oedema) of certain tissues. Without doubt the colloid chemistry of protein is of great importance in medicine.

Fruit jellies afford a familiar example of hydrated tissues. Pectin (a carbohydrate found in most fruits), sugar, and acid (with water) are essential to the formation of fruit jellies. Color and flavor are incidental. Apples are so rich in pectin that if this constituent is lacking in a given fruit, apples (or the white rind of citrus fruits) may be added. When acid is lacking in the fruit, sour grapes or lemon juice are often added.

A "*solid alcohol*" fuel may be prepared by quickly mixing about 85 volumes of 95 per cent alcohol with 15 volumes of a saturated aqueous solution of calcium acetate. The mixture "*sets*" to a solid jelly instantly. Cubes of it may be burned under a chafing dish. The commercial product is a cellulose ester-alcohol gel.

The most effective incendiary bombs we have used contained an oil jelly of mixed aluminum soaps that shattered, burning, over a wide area. The best flame throwers used some jellied petroleum which was projected as burning slugs.

Soaps. The alkali salts of oleic acid and of stearic, palmitic, and the other fatty acids are the soaps we commonly use. These soaps hydrate heavily. As a result commercial soap, although sold in solid cakes, contains surprising amounts of water. Soap flakes are dryer. However, the alkali salts of the unsaturated acids, such as oleic, hydrate much less than those of the saturated acids such as palmitic and stearic. In other words, a cake of soap made from cottonseed oil (liquid unsaturated fats) may contain less water

than a similar cake made from hydrogenated cottonseed oil (now saturated with hydrogen). Soaps of the type of sodium oleate (*genuine* castile) disperse better in cold water than do soaps of the saturated sort, such as sodium stearate or palmitate, and therefore cleanse better at ordinary temperatures. Naturally sodium oleate is preferable for toilet use. In the very hot water of laundries sodium stearate and the rest of its class are at their best. Soaps of calcium, magnesium, lead, and of all but the alkali metals hydrate very little, do not disperse well in water, and are therefore "insoluble." They are useless for cleansing. Lithium stearate does not disperse in water.

In soaps the colloidal properties are due to the long-chain anions — and their tendency to form colloidal aggregates — yet there are other colloidal substances in which it is the long-chain cation that performs a similar useful role. Synthetic detergents of this and other types now compete with soap.

Froths and Films. Adsorption films around the drops in emulsions have already been discussed. Films have, of course, but one colloidal dimension, thickness. When oleic acid, for example, dissolved in a volatile solvent, is poured on to the surface of water, it spreads, if permitted, to a film only one molecule thick.

Ore Flotation. A great increase in the amount of copper and zinc recovered from their sulfide ores is secured by the flotation process. An oily froth, by selective "wetting," floats the finely grouped particles of the mineral sulfides, while the waste rock, selectively "wetted" by water, sinks. Over 60,000,000 tons of ore are "floated" annually. Flotation froths are made semi-plastic by their coating of finely powdered sulfide ore, which adheres to the oil film.

Froth flotation is also applied to the concentration of many non-metallic minerals such as phosphate rock, coal, and feldspar.

A film of magnesium fluoride, in thickness one quarter the wave length of light, deposited on the surface of glass lenses cuts down the loss of light by surface reflection and eliminates glare.

Wetting of Solids by liquids is a phenomenon of great importance. Dye solutions must spread through or "wet" textiles uniformly and rapidly or the goods look spotty and uneven. A light skein of dry cotton sinks in cold water after an hour or so, yet if

only 0.2 of one per cent of isopropylnaphthalene sodium sulfonate or of Aerosol O. T. is added to the water the cotton sinks in a few seconds.

Sprays of fungicides must wet the green leaf which is to be protected, insecticides should wet insects, cattle dips should wet cattle hairs in order to reach the skin, and all sorts of liquids are called upon to wet all sorts of surfaces.

Some effective wetting agents are prepared by reducing long-chain fatty acids to alcohols which are then sulfated and neutral-

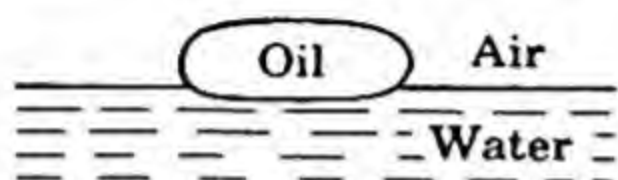


Fig. 130. A small amount of a hydrocarbon oil does not spread readily on water but takes a lens form.

ized with sodium carbonate. They even improve the absorptive capacity of towels, cleansing tissues, and blotting paper. "Wetter water" is a phrase with meaning. Sulfur powder floats in plain water but sinks at once in water containing 0.1 per cent Aerosol O. T.

Platinum wires form good air-tight seals in glass because glass, softened in the flame, "wets" platinum well. The General Electric Company saved \$7,500,000 yearly by substituting small copper or cobalt tubes (filled with a Ni-Fe alloy of the same coefficient of expansion as the glass). Glass wets the copper or cobalt surface just as well as it wets platinum and adhesion is excellent.

In the first mercury-power turbine there was poor contact of mercury and steel of the boiler because the liquid mercury failed to wet the steel well. A trace of titanium (lowering interfacial tension) cured the trouble.

Monomolecular Films. Although a drop of a liquid hydrocarbon floats on water as a lens there are large numbers of oils which when placed on water spread out to form extremely thin films of the order of 10^{-7} cm. thick. It is found that the general characteristic of all such substances that spread is that they contain in their molecules certain groups of atoms which have an affinity for water and are therefore called *hydrophilic*. Some common groups of this polar type are the —OH group and the —COOH group. If such a group is substituted for one of the hydrogen atoms in each of the molecules of a lower hydrocarbon, the effect is to increase the solubility of the substance in water.

The substances that spread as thin films upon water are thus substances whose molecules form a composite surface, most of the molecule (the hydrocarbon group) having very little affinity for water, thus being *hydrophobic*, while another portion of the molecular surface ($-\text{OH}$, $-\text{COOH}$, $-\text{NH}_2$, etc.) is *hydrophilic*. By spreading on the surface of the water, the molecules can thus arrange themselves so that the hydrophilic portion of each molecule comes into contact with water without bringing the hydrophobic portion in contact with the water. In the common fatty

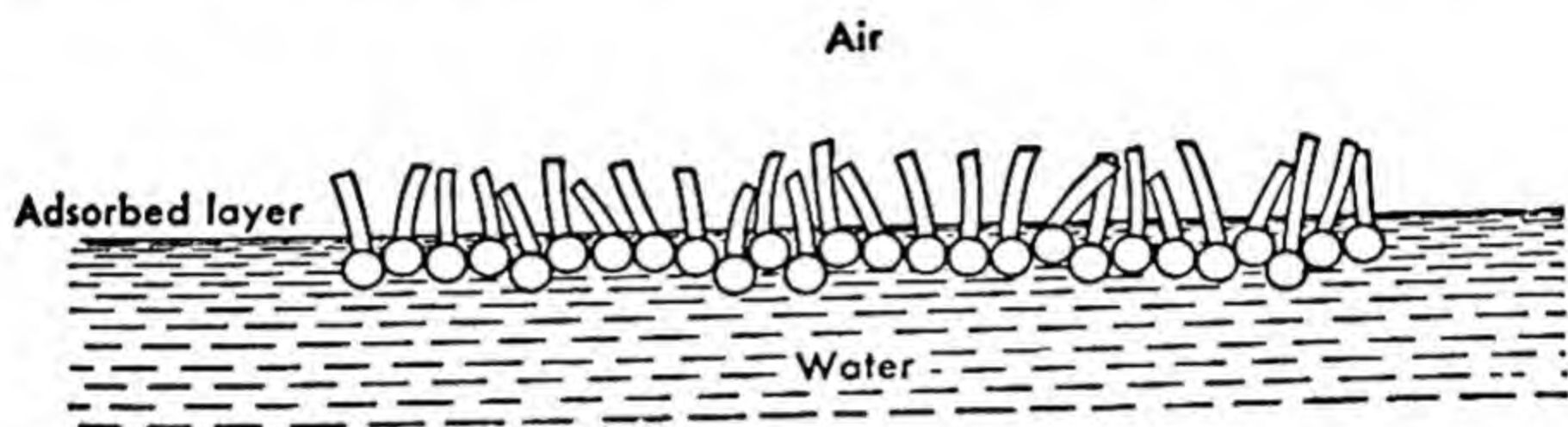


Fig. 131. Orientation of a fatty acid in the surface of water as a monomolecular film. The water-soluble polar group is attracted by the polar water, while the long hydrocarbon part of the molecule is repelled as insoluble.

acids (palmitic, stearic, oleic), the $-\text{COOH}$ group is at the end of the long chain of carbon atoms. Thus when the molecules spread over the surface of the water, they become oriented on the water so that they are approximately vertical with their heads (hydrophilic groups) in the water and their tails (hydrophobic groups) packed side by side above the layer that contains the heads.

By measuring the minimum volume of oil required to form a film just covering a given area, the thickness of the film can be calculated. This minimum thickness is evidently the length of the molecules, since these are arranged nearly vertically in the film. From such experiments it is possible to calculate the length and cross section of a polar molecule.

Smokes and Dusts. In one ml. of thick smoke there may be 5,000,000 solid particles. If magnified 1,000,000,000,000 times each particle would be 0.6 cm. in diameter and placed two feet from the others.

Filtration of dust or smoke-laden air through cloth bags (bag filters in the zinc oxide industry) or through felt or porous paper as in the gas mask is reasonably effective if the fibers are long, forming spiral paths. Glass-fiber mats are also used. Toxic smokes in warfare are stopped by a layer of felt in the gas mask.

City fogs are persistent because of a film of soot or tarry material (from coal smoke) on the outside of each drop. This checks evaporation. On a single square mile of some of our large cities the fall of dust and smoke in a year is as much as 1500 to 2000 tons.

In some factories, where dust interferes seriously with the quality of products, electrical precipitators remove this dust from air very effectively.

The dust-laden air passes through a set of fine wires charged to 15,000 volts by direct current. Dust particles take this charge and are discharged against a series of grounded metal plates.

Smelter fumes are treated in this manner and if the ores carry arsenic it is precipitated, and recovered, as the trioxide. Some cement kilns reduce dust losses by this device.

Ultra-high frequency sound waves also precipitate dusts and fumes.

Soils. The productivity of a soil is closely related to its colloid content. Weathering of feldspar yields much colloidal material in the form of alumina and silicic acid. This, with colloidal hydrated oxides of iron and with humus, gives soil the proper physical condition. Humus is an indefinite mixture of organic substances, the débris of bacteria, plants, and animals. It acts as a protective colloid tending to keep much of the soil in the hydrosol state.

Exercises

1. Why do the heavy particles of red colloidal gold not sink in water?
2. How could you remove the negative charge from a negative colloid?
3. Why do some precipitates run through a filter paper on prolonged washings?
4. Give several examples of adsorption from liquids. From gases.
5. How could you make an emulsion of carbon tetrachloride-in-water or of water-in-carbon tetrachloride at will?

6. How could you break an emulsion?
7. Explain the cleansing action of soap.
8. A good colloidal solution of red ferric hydroxide is clear and runs through the best filter paper. How could you prove that it is colloidal and not a true solution?
9. Prove that the spreading of liquids on solids is important.
10. Explain ore flotation.
11. How can you prepare a monomolecular film, and measure its thickness?
12. How does silica gel dry gases?
13. How can dust, smoke and mist be removed from air?

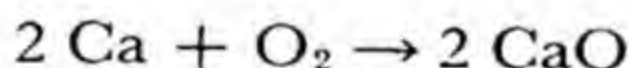
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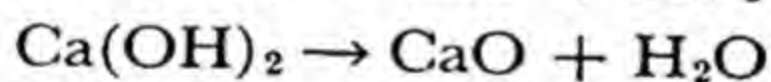
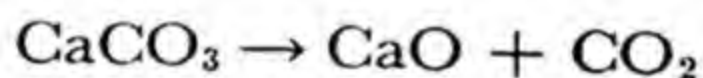
Chapter 36 COMPOUNDS OF THE METALS

GENERAL METHODS OF PREPARATION

Preparation of Oxides. The simplest, but not most economical, method of preparing metallic oxides is the heating of the more active metals in air. (See page 99.)

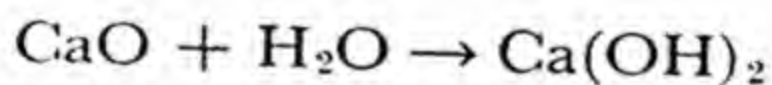


It is usually better to heat the carbonate, hydroxide or nitrate:

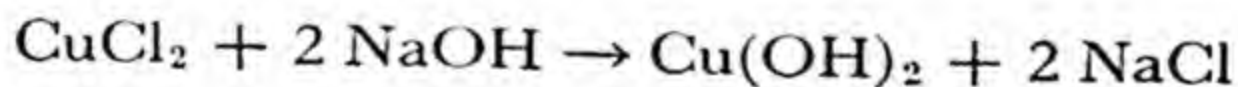


The nitrates of the sodium group do not yield oxides on dry ignition.

Preparation of Hydroxides. A few oxides (of more active metals) are readily hydrated to the hydroxides:

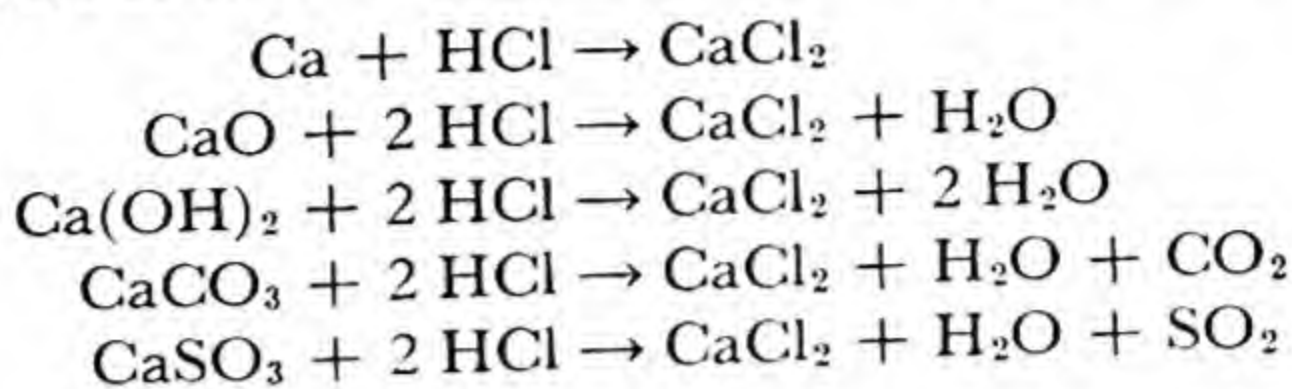


Precipitation of the desired hydroxide by addition of sodium hydroxide, etc., to a solution of the appropriate salt is convenient:



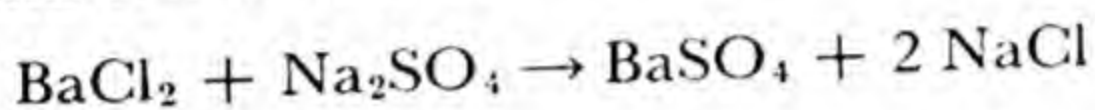
The preparation of NH_4OH by reaction of NH_3 with water is exceptional.

Preparation of Salts. Action of the appropriate acid on the metal (if not too inactive, like platinum), or on the metallic oxide or hydroxide or carbonate or sulfite usually yields the salt desired:

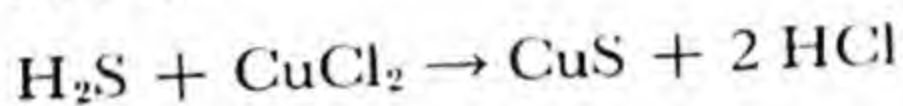


To this list may be added the direct attack of halogens on most metals.

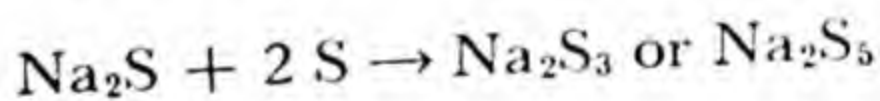
Solutions of two salts may be mixed if one of the products is insoluble and can be filtered.



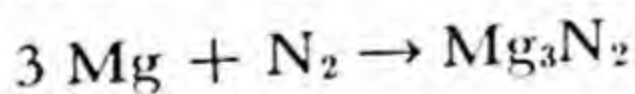
Sulfides are formed by heating the metal with sulfur ($\text{Fe} + \text{S}$), or by adding H_2S or Na_2S or other soluble sulfide to a solution of the appropriate salt



and **polysulfides** may be prepared by warming simple sulfides with sulfur:



Nitrides result with a few active metals when they are heated in nitrogen (absence of oxygen):

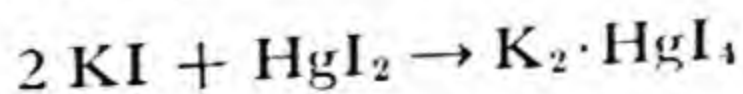


Carbides (abrasives such as "carborundum," etc.) are discussed on page 133.

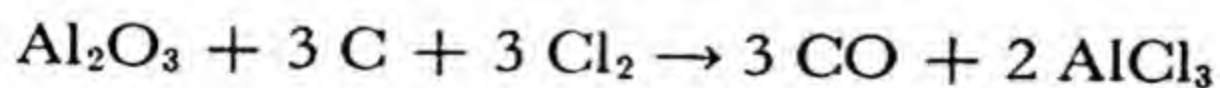
Soluble complex cyanides are formed whenever simple insoluble cyanides are treated with an excess of KCN or NaCN solution:



Similarly some **complex, soluble iodides** result from the use of an excess of KI or NaI solution:



Some anhydrous chlorides have been prepared industrially by joint attack of hot carbon and chlorine on the metallic oxide. For example, aluminum chloride.



Hydrides are usually formed by direct action of hydrogen on the more active metals (hot and in absence of air). Calcium hydride, CaH_2 , is valuable in reducing refractory oxides, such as TiO_2 , and as a drying agent. Lithium-aluminum hydride, LiAlH_4 , recently prepared, is a white solid of unique reducing powers toward organic compounds.

Reference

Gibb, T. R. P., "Hydrides," *J. Chem. Education*, 25, 577 (1948).

Chapter 37 COMPOUNDS OF THE ALKALI METALS

SOME SODIUM COMPOUNDS

(The metal is discussed on pages 206 and 207.)

FORMULA	NAME	SOLUBILITY IN WATER	REMARKS
NaCl	Sodium chloride	Soluble	Source of chlorine, NaOH, Na ₂ CO ₃ , etc.
NaNO ₃	Sodium nitrate (Chile saltpeter)	Very soluble	Fertilizer. One source of HNO ₃
NaNO ₂	Sodium nitrite	Very soluble	Used in making dyes, pickling meats
Na ₂ CO ₃	Sodium carbonate	Soluble	In manufacture of glass, soap, paper; water softening
Na ₂ CO ₃ · H ₂ O	Sodium carbonate monohydrate	Soluble	
Na ₂ CO ₃ · 10 H ₂ O	Sodium carbonate decahydrate (washing soda)	Soluble	
NaHCO ₃	Sodium bicarbonate (baking soda)	Soluble	In preparation of baking powders
NaOH	Sodium hydroxide (caustic soda)	Very soluble	Cheapest strong base. In preparation of soap, viscose rayon, reclaimed rubber, etc.
Na ₂ SO ₄ · H ₂ O	Sodium sulfate	Soluble	In glass and paper making
Na ₂ SO ₃	Sodium sulfite	Soluble	In photography. Antichlor for bleached textiles
NaHSO ₃	Sodium bisulfite	Soluble	In chrome tanning, making dyestuffs
Na ₂ S ₂ O ₃	Sodium thiosulfate (hypo)	Soluble	In photography. Removes unused silver bromide
Na ₂ S ₂ O ₄	Sodium dithionite	Soluble	Reduces indigo to soluble indigo white for textiles
Na ₂ S	Sodium sulfide	Very soluble	Dehairs hides. Denitrates nitrocellulose rayon
NaCN	Sodium cyanide	Soluble	Forms soluble complex cyanide of gold in ores. Source of HCN, fumigation of orange trees
NaBO ₃	Sodium perborate	Soluble	Bleaching agent in washing powders. Releases H ₂ O ₂

Similar compounds of potassium, ammonium, lithium, rubidium and cesium have been made. Sodium compounds are the cheapest.

LITHIUM COMPOUNDS

Half of the lithium salts produced in this country come from the brine of Searles Lake, California. Lithium compounds in some respects resemble calcium compounds more than one might expect. The carbonate, Li_2CO_3 , has some use in glass and ceramics while lithium soaps find growing use in special lubricating greases. Lithium stearate, unlike soaps of other alkali metals, does not disperse in water. The lithium ion, unlike hydrogen, is highly hydrated. Lithium aluminum hydride was mentioned in the previous chapter.

Lithium chloride (LiCl) solutions have some use in controlling relative humidity of air. Lithium salts color flames a vivid crimson.

SODIUM COMPOUNDS

(The metal is discussed on page 206.)

Sodium Chloride. Common salt, NaCl , is the natural source of all sodium compounds although some natural deposits of sodium carbonate, sodium sulfate, sodium nitrate, and sodium borate are used. Fortunately for the human race this necessary mineral is plentiful in most countries. The ocean carries over 3 per cent solids and Great Salt Lake more than 20 per cent. Great beds of solid salt are found in Europe and in several districts of the United States. Deep beds are usually tapped with wells and, if necessary, water is introduced to form a brine, or they are mined.

Salt crystallizes in cubes with hollow faces. It melts at 803° and volatilizes at high temperatures. As the chief source of sodium compounds and of chlorine, as a food preservative, and as an essential article of diet sodium chloride is of major importance. It is startling to learn that the average man eats 10 pounds of salt yearly in his food.

The United States alone produced 16,000,000 tons of salt in 1947.

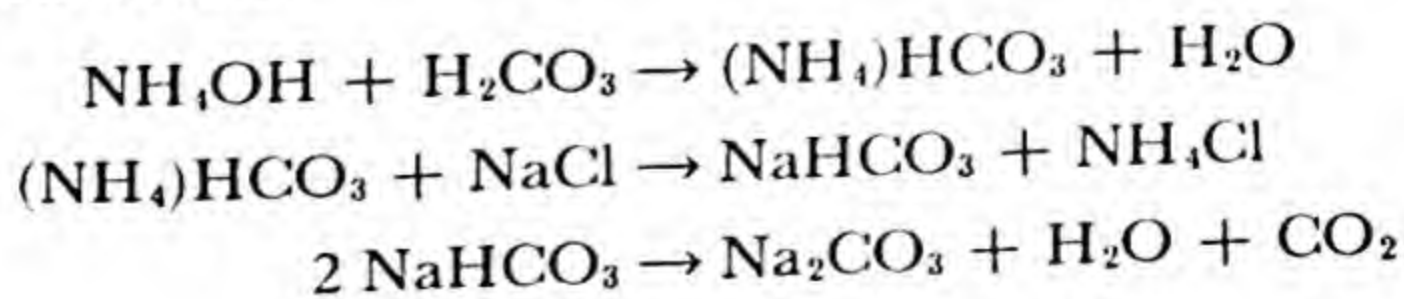
Sodium Nitrate, NaNO_3 , is discussed on page 361 and the phosphates on page 377.

Exercise

1. From Chapter Thirty-one learn the method of detecting the difference between a nitrate and a nitrite.

Sodium Carbonate, or "Soda Ash," Na_2CO_3 . Although there are some lake deposits in California and East Africa practically all of this salt used before 1791 was obtained from the ashes of sea plants (land plants yield potassium carbonate on burning). Naturally sodium carbonate was expensive and, as a result, so were glass and soap. It is scarcely an exaggeration to say that the progress of civilization was greatly retarded for want of a cheap source of sodium carbonate. Just prior to the Napoleonic wars France was deprived of its usual supply, so the French Academy offered a prize of 100,000 francs for the discovery of a method for manufacturing an adequate supply from common salt. LeBlanc rose to the occasion. His process ($\text{NaCl} \rightarrow \text{Na}_2\text{SO}_4 \rightarrow \text{Na}_2\text{S} \rightarrow \text{Na}_2\text{CO}_3$) was used for a century but was finally displaced by the more efficient Solvay process.

The Solvay Process. The LeBlanc method had no rival until 1863, when the Belgians, Ernest and Alfred Solvay, achieved success with their ammonia-soda process. In the Solvay process concentrated sodium chloride solution is saturated with ammonia and carbon dioxide. At first ammonium bicarbonate, $(\text{NH}_4)\text{HCO}_3$, is formed and this reacts with sodium chloride to form sodium bicarbonate. The latter salt, only sparingly soluble in the salt solution, precipitates, and after removal is heated to form sodium carbonate:



The process is carried on in steel towers about 50 feet high and 6 feet wide with numerous shelves and water traps to insure thorough mixing. The gases are led in at the bottom, and half-way up the side. The temperature in these carbonating towers is not allowed to rise above 35°C .

The economy of operation is great. Instead of wasting the ammonium chloride produced it is heated with lime to release ammonia gas, which, of course, is passed into the towers again. And

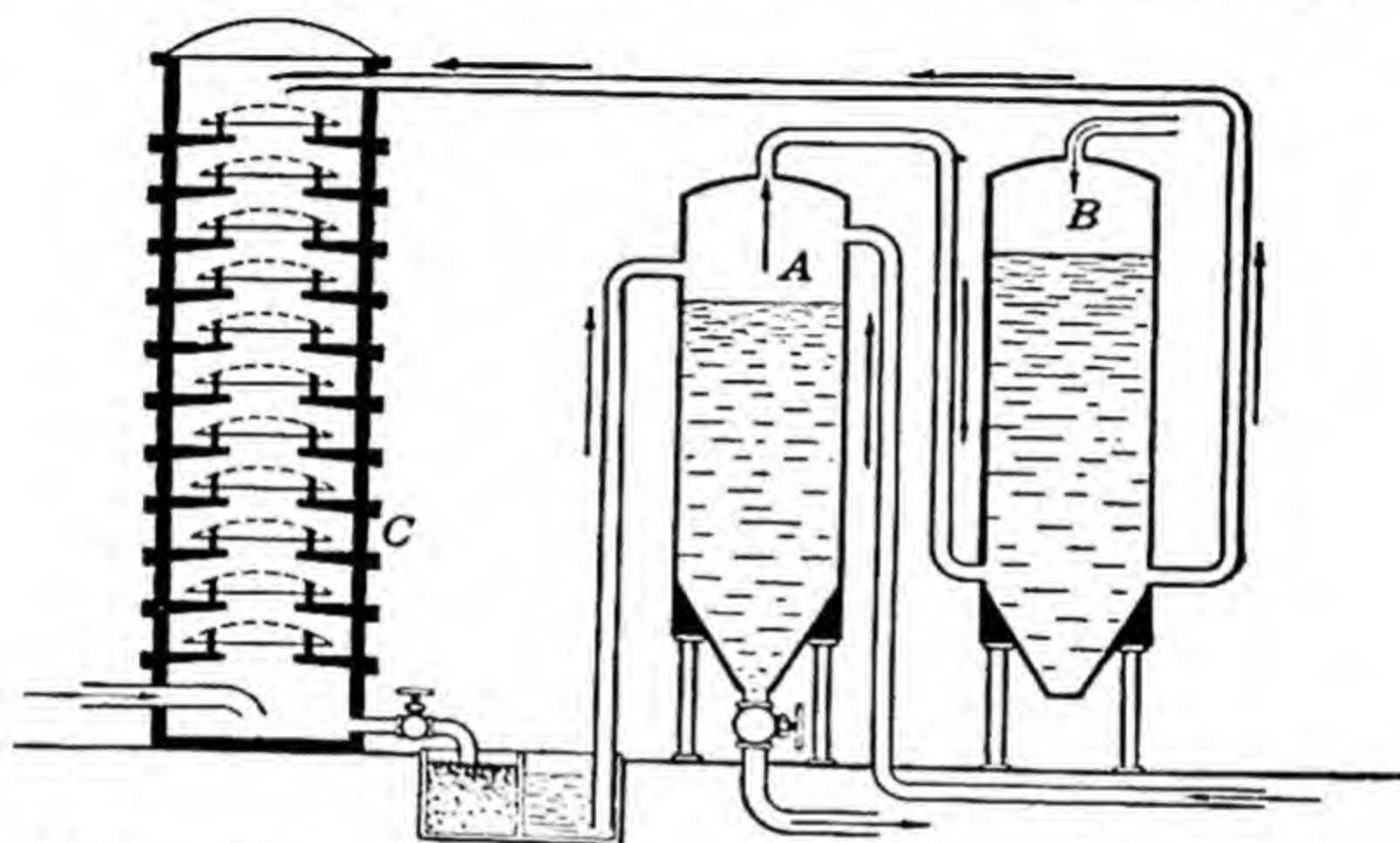
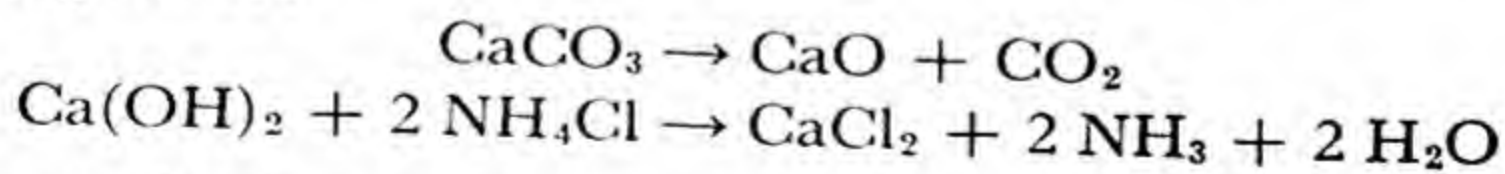


Fig. 132. Solvay soda process. The ammonium chloride solution from the tower *C* is pumped into a cylinder *A* where it is mixed with lime water. The escaping ammonia gas is led into a cylinder *B* of salt brine which is then pumped into the carbonating tower *C*.

instead of buying this necessary lime in the open market it is made at the plant by heating limestone to about 900° . The carbon dioxide released from the calcium carbonate is used in the carbonating tower:

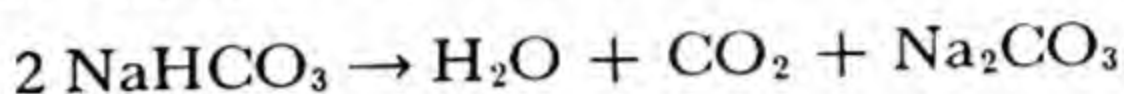


The production in the United States in one recent year was 285,000 tons of natural soda and more than 4,500,000 tons of Solvay soda. It is essential to many important industries, such as the manufacture of glass, soap, paper, leather, enamels. It is also used in cleansing, water softening, dyeing, and oil refining. Syn-

thetic soda, cheaper and purer than that obtained from ashes of marine grasses, revolutionized glass making.

2. Draw a sodium carbonate tree, root and branch, to show sources as roots, and products and uses as branches. (See the coal tar tree, page 609.)

Sodium Bicarbonate, NaHCO_3 . This so-called baking soda is the direct product of the Solvay process. About one ton out of every seven is sold in that form to be used in baking powders, in medicine, etc. The rest is heated to secure the normal carbonate:



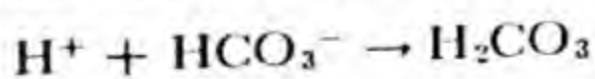
The CO_2 evolved, together with more from limestone, is used to make more NaHCO_3 .

Although Na_2CO_3 solutions are strongly alkaline by hydrolysis, NaHCO_3 solutions are not appreciably alkaline. Due to increased hydrolysis upon heating, warm NaHCO_3 solutions turn phenolphthalein pink. From the formula the student may expect hydrogen ions, but the HCO_3^- ion is very stable.

Lecture Experiment. If to concentrated ammonia water saturated with sodium chloride a lump of solid carbon dioxide is added, a copious precipitate of sodium bicarbonate is obtained in ten minutes. The experiment works well in a 2-inch cylinder, about half-filled.

3. Represent by equations the hydrolysis of sodium carbonate.

Baking Powders. To secure plenty of surface in dough, thus making the product "light," some gas must be released throughout the mixture. Air would do, but it is more convenient to have carbon dioxide released. This can be accomplished by addition of a harmless acid (or acid salt) to baking soda. Lactic acid of sour milk has been used with uncertain results when the amount added was not exactly equivalent to the soda. Cream of tartar baking powders serve the purpose very well. They are mixtures of acid potassium tartrate and sodium bicarbonate. The hydrogen ions from the acid salt unite with the HCO_3^- ions from the sodium bicarbonate to form carbonic acid, which breaks down into water and carbon dioxide:



Phosphate baking powders contain an acid phosphate (monocalcium phosphate). "Alum" baking powders depend upon the acid reaction caused by hydrolysis in alum solutions. As a matter of fact common alum is not used but, instead, anhydrous sodium aluminum sulfate or $\text{NaAl}(\text{SO}_4)_2$. This, how-

ever, makes no difference in the physiological effects which are probably negligible. With all the baking powders described above the salts left in the food are harmless unless used in excessive quantities.

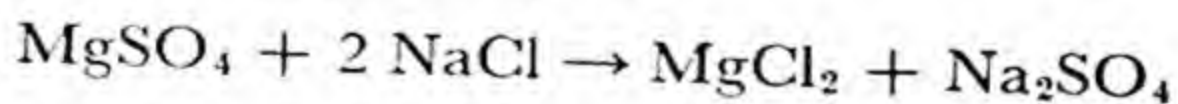
The phosphate-sulfate type is the most popular. A phosphate baking powder in the cold is rapid enough and progressive enough in its action to prepare the dough for the oven while the more slowly soluble sulfate keeps the carbon dioxide evolving until the dough is set by heat.

A cream of tartar powder gives off its carbon dioxide too well in the early part of the operation, so jarring or slow baking may spoil things.

Sodium Hydroxide, NaOH. This base, of which we use over 2,000,000 tons annually, was discussed on page 207.

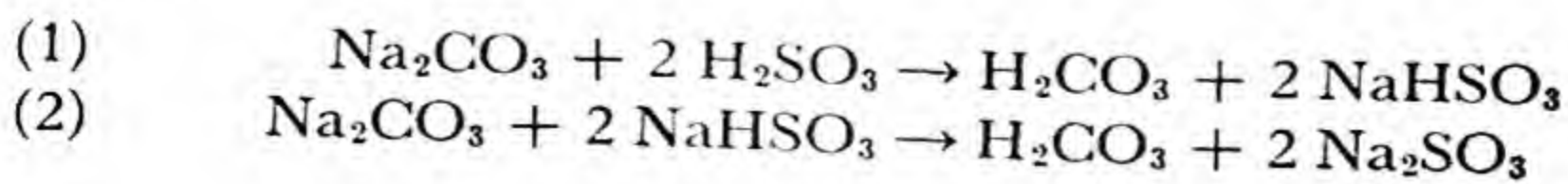
Sodium Sulfate, Na₂SO₄. Unlimited quantities of this salt are found in Siberian lakes, in Canada, in a bay of the Caspian Sea, and in North Dakota; and great deposits fully 98 per cent pure are located in dry lake beds in the southwestern part of the United States. In a recent year 170,000 tons of natural Na₂SO₄ were produced in this country.

Glauber, the alchemist, used it in medicine as early as the middle of the seventeenth century, hence the name Glauber's salt. It crystallizes below 32.38° as Na₂SO₄ · 10 H₂O and above this transition point as the anhydrous salt, Na₂SO₄. Considerable quantities are used in glass making and in making paper from certain woods such as southern pine. Our annual needs for this and for the dye industry total nearly 1,000,000 tons. At Stassfurt, Germany, the magnesium sulfate obtained as a by-product in separating potassium chloride from the great bed of salts is mixed with a solution of sodium chloride:

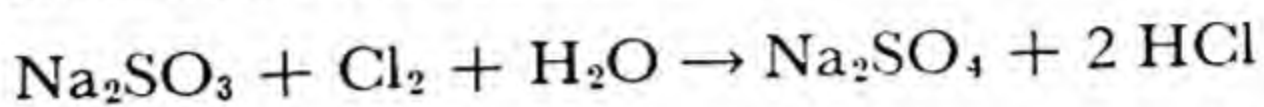


The sodium sulfate is the least soluble of the four salts and crystallizes out when the solution is concentrated and cooled.

Sodium Sulfit, Na₂SO₃. The sulfite of sodium is obtained by saturating a solution of the carbonate with sulfur dioxide and then adding an amount of the carbonate just equal to that taken at first:

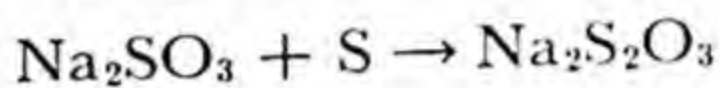


It is used in photography and as an *antichlor* in the textile industry. Chlorine left in the fabric after bleaching weakens the fibers, but if sodium sulfite is added the chlorine reacts to form harmless salts. Sulfites readily oxidize in the air, so they are apt to be contaminated with sulfate. They are good reducing agents.

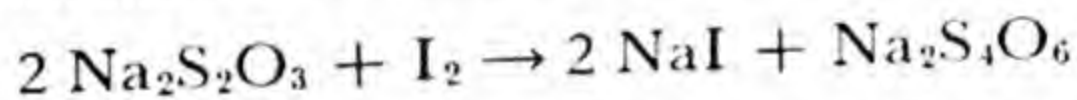


Sodium bisulfite, NaHSO_3 , is the product of reaction (1). It is used in paper making, chrome tanning, the making of dyestuffs, and as an antichlor.

Sodium Thiosulfate, $\text{Na}_2\text{S}_2\text{O}_3$. Photographers know this compound as "hypo" and use it to dissolve unused silver bromide from the developed plates. It is formed very easily by boiling sodium sulfite with sulfur:



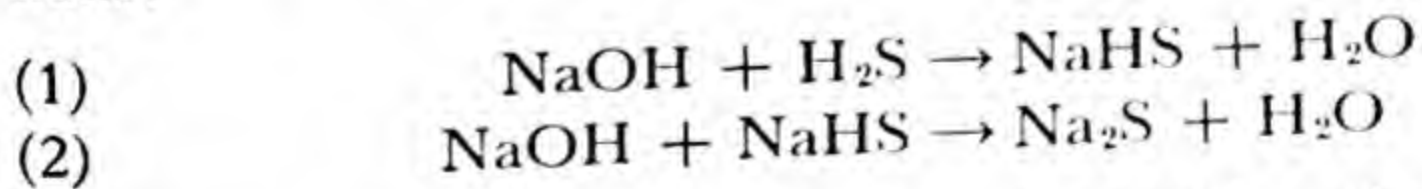
The salt is used in quantitative determination of free iodine because it reacts with iodine to form colorless compounds, sodium iodide and sodium tetrathionate:



4. If a solution of iodine in potassium iodide is added to sodium thiosulfate, what color change takes place? Write the equations.

Sodium dithionite, $\text{Na}_2\text{S}_2\text{O}_4$, a powerful reducing agent for indigo dye, was discussed on page 275.

Sodium Sulfide, Na_2S . The laboratory preparation consists in dividing any solution of sodium hydroxide into two equal parts, saturating one with hydrogen sulfide and mixing the two portions:

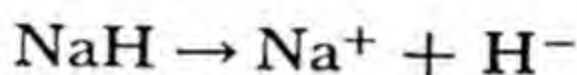


Commercial reduction of sodium sulfate with carbon at 900° also yields sodium sulfide, which is also a by-product of the barium sulfate industry. It is a very soluble crystalline salt. In solution it is strongly basic, due to hydrolysis, since it is a salt of a strong base and a weak acid. It is a necessary aid to the "sulfur colors" in

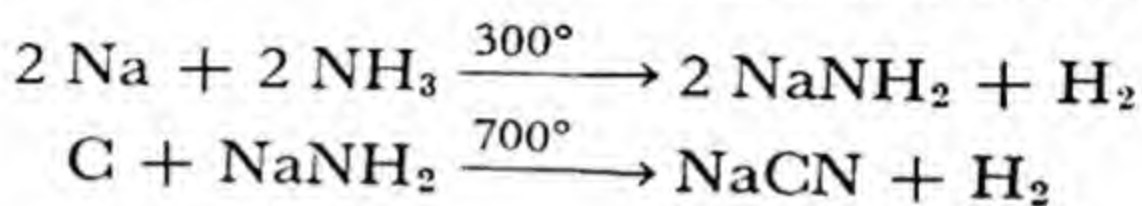
dyeing cotton and is also required in the manufacture of certain dyes. Its solution removes hair from hides and denitrates nitro-cellulose rayon. When a sodium sulfide solution is heated with sulfur, certain polysulfides of sodium are formed.

Sodium Hydride, NaH. This gray white crystalline powder, prepared by passing hydrogen over sodium at 250° – 300° is now coming into use in removal of oxide scale (by reduction) from steel. For this purpose the hydride is dissolved in fused sodium hydroxide.

It also dissolves in the fused eutectic mixture (352°) of 40 : 60 potassium chloride and lithium chloride. Upon electrolysis below the decomposition voltage of either component the NaH is decomposed, yielding hydrogen at the anode — not at the cathode as usual.

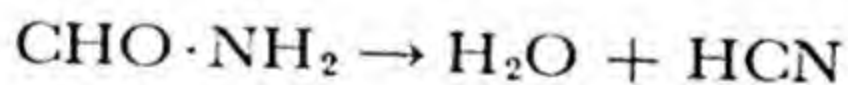


Sodium Cyanide, NaCN. A common method of preparing sodium cyanide involves the use of sodamide, NaNH_2 .



It is important to produce cheap sodium cyanide because it is much used in extracting gold from low-grade ores. Cyanides are also important in electroplating, case-hardening of steel, and as a fluxing material. Prussic or hydrocyanic acid (HCN) is used to fumigate citrus trees.

Germany has been making hydrocyanic acid by heating formamide and ammonia with aluminum phosphate as catalyst, at 350° – 370° .



Tests for Sodium Compounds. There are no insoluble sodium salts except sodium uranyl acetate, the fluosilicate, and the pyro-antimonate, $\text{Na}_2\text{H}_2\text{Sb}_2\text{O}_7$. Sodium salts are recognized by the intense yellow color they give to a colorless flame. As a rule sodium is reported in qualitative analysis only if there is a very intense and prolonged coloration of the flame. With the spectroscope the element is recognized by characteristic yellow lines.

Ten ml. of a uranyl zinc acetate solution, prepared by dissolving 4 grams of uranyl acetate and 15 grams of zinc acetate in 50 ml. of water acidified with 1 ml. of glacial acetic acid, will precipitate completely 8 mg. of sodium, if present, from 1 ml. of a solution of sodium salts in 1 hour. This ratio of 10 ml. reagent to 1 ml. of test solution must be used.

POTASSIUM COMPOUNDS

(The metal is discussed on page 530.)

Potassium Chloride and Other Compounds. The chloride is found nearly pure as sylvite in the Stassfurt deposits. Still more is obtained from these deposits by cooling a hot, saturated solution of carnallite, $\text{KCl} \cdot \text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$. The less soluble potassium chloride crystallizes out.

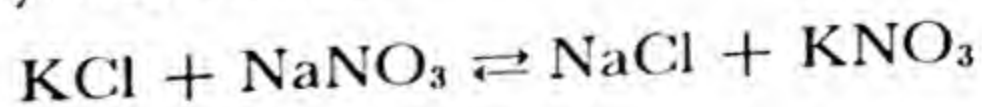
Fertilizer Salts. Depleted soils require the addition of potassium chloride or sulfate for permanent agriculture. In the past we imported great quantities of such salts mined at Stassfurt, Germany, in France, and in Spain. Now our needs of 900,000 tons (estimated as K_2O) are met by the Searles Lake and New Mexico deposits.

Searles "Lake" in the Mojave desert of California is a bed of crystallized salts about twelve square miles in area, 60 to 70 feet deep, and saturated with brine containing millions of tons of salts. The greater part of our production now comes from the Carlsbad deposit in New Mexico.

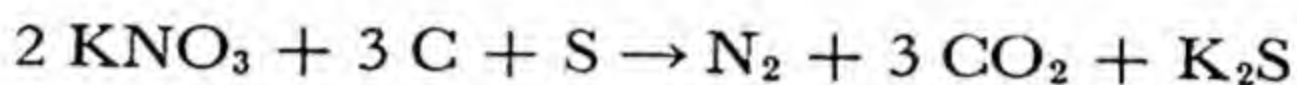
The mixture of sylvite and halite mined in New Mexico at 1000-ft. depths is hot-leached with water to dissolve out the potassium chloride. On cooling, a product averaging 98.5 per cent KCl is obtained.

Wood ashes have always furnished a moderate amount of potassium carbonate (the "lye" of colonial days) and small deposits of potassium nitrate are known.

Potassium Nitrate. Potassium nitrate has long been used in gunpowder. It was formerly obtained in small deposits in Bengal, hence the name, Bengal saltpeter. Scheele discovered oxygen by heating this salt. It is now prepared by mixing saturated hot solutions of sodium nitrate and potassium chloride. After the sodium chloride precipitated is filtered off, on cooling the filtrate potassium nitrate crystallizes out:



It forms rhombic crystals melting at 345° . Some of it is used in medicine, some to preserve meat, which it colors red, but most of it is still used in black gunpowder. This explosive is essentially 75 parts potassium nitrate, 10 parts sulfur, 14 parts charcoal, and 1 part water. It is mixed and ground wet and then dried carefully. On explosion, expanding gases form. The smoke is due to solid potassium sulfide:



Potassium Carbonate. Potassium carbonate is prepared by heating a mixture of magnesium carbonate and potassium chloride. Its chief use is in the making of hard glass.

Potassium Tetroxide. Unlike sodium, potassium unites with oxygen to form a tetroxide, K_2O_4 which with acid yields hydrogen peroxide and oxygen. Friction has exploded K_2O_4 in contact with potassium.

Tests for Potassium Compounds. The potassium flame is violet, but is easily masked by the intense yellow of the sodium flame. It is well to view the flame through a thick blue glass, which cuts off the yellow light. If perchloric acid is added to a solution of a potassium salt, white potassium perchlorate, KClO_4 , is precipitated, particularly in the presence of alcohol.

The potassium ion unites with the chloroplatinate ion to form insoluble potassium chloroplatinate, K_2PtCl_6 , in yellow octahedra.

Cesium and rubidium compounds, resembling the group, have few uses.

AMMONIUM SALTS

Ammonium Chloride, NH_4Cl . This salt crystallizes in cubes or octahedra. At 350° it dissociates into ammonia and hydrogen chloride. On cooling the gases unite to form a smoke of ammonium chloride. The equilibrium is displaced by change in temperature:

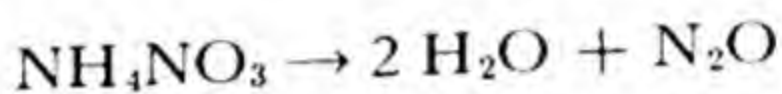


The addition of either HCl or NH_3 would disturb the equilibrium to the left. Better "opportunity for contact" between the two

gases accounts for this. "Mass action" is another phrase for the same thing. The salt is made by passing ammonia into hydrochloric acid or by heating together ammonium sulfate and sodium chloride. Its use in soldering depends on its ability to clean off oxides, allowing metallic surfaces to be brought into contact. Its largest use is in the manufacture of over 500,000,000 dry cells each year in the United States alone.

Ammonium Sulfate, $(\text{NH}_4)_2\text{SO}_4$. The sulfate is a product of coke manufacturing (see page 130). Ammonia is passed directly into sulfuric acid, forming this salt. As a source of nitrogen in fertilizers it is needed annually to the extent of half a million tons in this country alone.

Ammonium Nitrate, NH_4NO_3 . There are five transition points of this salt, at -16° , 32° , 85° , 126° , and 169° . It melts at 160° and at higher temperatures decomposes into water and nitrous oxide:



Most ammonium salts on heating yield ammonia, but ammonium nitrate is an exception. It may explode if heated too rapidly. In fact it is mixed with some explosives. This salt has some use in fertilizers.

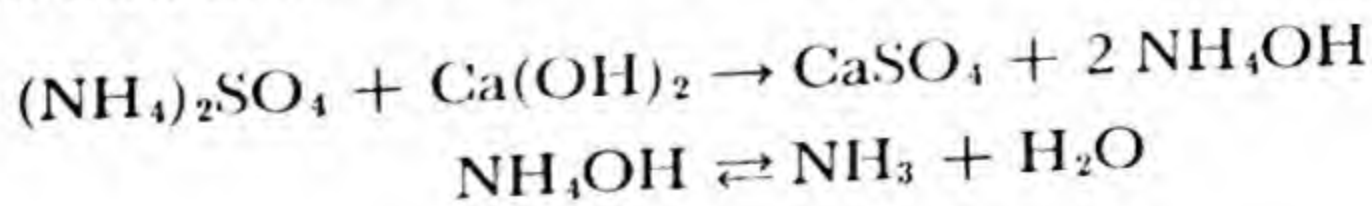
A few years ago a fire broke out on a ship loaded with 2,500 tons of ammonium nitrate, docked at Texas City. A disastrous explosion resulted wrecking ships and also industrial plants on shore. In contact with combustible material this salt is a hazard.

Ammonium Sulfide, $(\text{NH}_4)_2\text{S}$. This analytical reagent is prepared by passing hydrogen sulfide into ammonium hydroxide.

Ammonium Hydroxide, NH_4OH . This weak base is discussed on page 345.

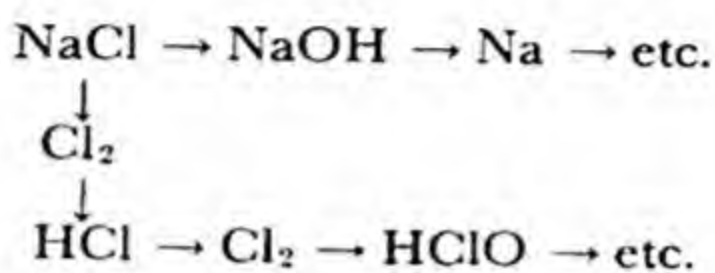
Ammonium amalgam. $\text{NH}_4\text{Cl} + \text{NaHg} \rightarrow \text{NH}_4\text{Hg} + \text{NaCl}$

Tests for Ammonium Salts. All ammonium salts on warming with a base give off ammonia gas, recognized by odor and by its ability to turn moist red litmus paper blue:



Exercises

5. Assuming 90 per cent recovery, what weight of baking soda will be obtained by the Solvay process from 247 kg. of common salt?
6. Sodium carbonate solutions are basic. Why not boil such a water solution counting on hydrolysis and the decreased solubility of carbon dioxide at higher temperatures to convert all the sodium carbonate into the more valuable sodium hydroxide?
7. How much sodium chloride would be necessary for the preparation of 1 ton of sodium hydroxide?
8. Extend this chart:



9. If you passed CO_2 continuously into a tank of salt water (cathode compartment) which was being electrolyzed, what product would you get?
10. What are the useful properties of sodium hydride?

References

- Lange, N. A., ed., *Handbook of Chemistry*, 6th ed. Sandusky, Ohio, Handbook Publishers, Inc., 1946.
- Smith, H. I., "Potash in the Permian Salt Basin." *Ind. Eng. Chem.*, 30, 854 (1938).

Chapter 38 COMPOUNDS OF THE ALKALINE EARTH METALS

Calcium, Barium, Strontium, Magnesium,
Beryllium, and Radium

SOME COMPOUNDS OF CALCIUM, BARIUM, AND STRONTIUM

(The metal calcium is discussed on page 533.)

FORMULA	NAME	SOLUBILITY	REMARKS
CaO	Calcium oxide (quicklime)	Reacts with water	A cheap base-former. Reacts with H ₂ O and CO ₂ of the air
Ca(OH) ₂	Calcium hydroxide (slaked lime)	Slightly soluble	Used as "milk of lime," a suspension in water
CaCO ₃	Calcium carbonate	Insoluble	Source of CaO. Occurs as limestone and marble
Ca(HCO ₃) ₂	Calcium bicarbonate	Soluble	Formed from CaCO ₃ by action of CO ₂ and H ₂ O
CaCl ₂	Calcium chloride	Very soluble	Anhydrous form is a powerful air drier. Used to lay dust on roads
CaSO ₄ · 2 H ₂ O	Calcium sulfate (gypsum)	Slightly soluble	Used in plaster casts, etc.
BaO	Barium oxide	Reacts with water	Source of BaO ₂
BaO ₂	Barium peroxide		One source of H ₂ O ₂
Ba(OH) ₂	Barium hydroxide	Soluble	Little commercial use
Ba(NO ₃) ₂	Barium nitrate	Very soluble	Used in pyrotechnic signals (green)
BaCl ₂	Barium chloride	Soluble	Various uses
BaSO ₄	Barium sulfate	Very soluble	Precipitated form ("blanc fixe") is a filler in paper, litho- graph inks, etc.

Continued on the following page

438 COMPOUNDS OF ALKALINE EARTH METALS

FORMULA	NAME	SOLUBILITY	REMARKS
$\text{Sr}(\text{OH})_2$	Strontium hydroxide	Soluble	Once used in sugar purification (Europe)
SrCO_3	Strontium carbonate	Insoluble	A source of other salts
SrSO_4	Strontium sulfate	Insoluble	
$\text{Sr}(\text{NO}_3)_2$	Strontium nitrate	Very soluble	Used in red signal lights

CALCIUM COMPOUNDS

Calcium Carbonate. Vast beds of limestone are found in most countries. Other forms of the carbonate are marble (composed of small calcite crystals) and chalk. Marl is a mixture of limestone and clay. Chalk is made up of the skeletons of minute marine organisms. Sea-shells, corals, pearls, and egg-shell are familiar forms of calcium carbonate.

Pure crystallized calcium carbonate is found in two forms, aragonite and calcite, differing in crystal shape and density. When the carbonate is formed in solutions above 30° aragonite crystals deposit, but below 30° calcite crystals are obtained.

Calcium carbonate is practically insoluble in water, as one liter holds only 13 mg. of the salt. But when water is saturated with carbon dioxide the solubility of the carbonate increases thirtyfold. To be exact, the bicarbonate is formed:



Rain washes the carbon dioxide of the air into the soil and as this carbonated water trickles over beds of limestone the soluble bicarbonate forms and the water becomes "hard." In many places underground caves are formed in this manner. Some springs deposit this dissolved rock when the sudden decrease of pressure on the water allows the escape of carbon dioxide.

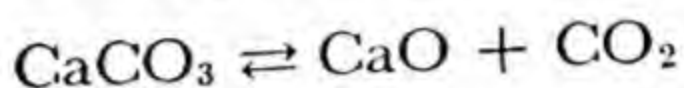
A good lecture experiment follows:

"An unfrosted light bulb is set up in series with a pair of copper electrodes dipping into 40 ml. of distilled water in a 100 ml. beaker. Upon adding 2 ml. of saturated $\text{Ba}(\text{OH})_2$ solution, the lamp shows good conductance. Carbon dioxide is now bubbled through the solution; the light gradually goes out and then comes on again as the soluble bicarbonate is formed."

Arenson.

Limestone has many uses. It is quarried in great quantities as a source of lime and for the manufacture of cement, glass, and ceramic material. Modern agriculture approves the use of ground limestone as well as lime in correcting the acidity of soils. Calcium carbide and cyanamide both require limestone or lime as a raw material. Great quantities of limestone are used in getting iron from its ores.

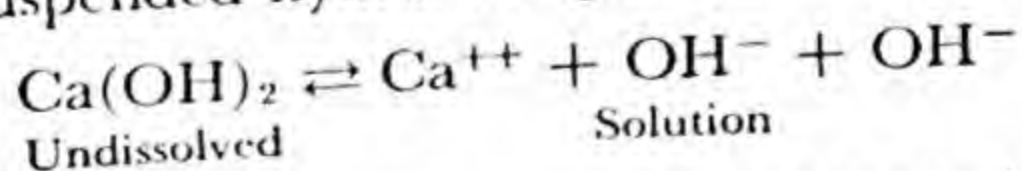
Calcium Oxide, CaO . This oxide, known as quicklime, is usually obtained by heating limestone to about 900°C . in gas-fired kilns:



Calcium oxide is a white solid melting at about 2750° and boiling at higher temperatures. Heated by the oxyhydrogen flame it becomes brilliantly incandescent and was once used as a source of light for lantern projection (the "lime light"). Calcium oxide is very difficult to reduce. Potassium and sodium are able to reduce it only at the temperature of the electric furnace.

Lime, our cheapest base, has uses to the extent of more than 6,000,000 tons in this country in the preparation of paper, rubber, sand-lime bricks, calcium carbide and acetylene, lime-sulfur sprays, calcium arsenate dust for cotton crops, Bordeaux mixture, and in the clarification and softening of water.

Calcium Hydroxide, $\text{Ca}(\text{OH})_2$. Slaked lime is a white powder formed by the careful addition of water to quicklime. It is slightly soluble, 100 ml. of water dissolving 0.17 g. at 18° . At higher temperatures it is less soluble. The little that is in solution ionizes rather well, but when considerable quantities of a base are required it is customary to use a suspension of the solid in water known as "milk of lime." As fast as the little in solution is used up some of the suspended hydroxide goes into solution:



This is the cheapest base known and has many industrial uses. In making mortar, plaster, alkalies, bleaching powder, purifying illuminating gas, removing hair from hides, and clarifying sugar solutions it is important. Naturally some of these uses duplicate those for the oxide.

Mortar. Mortar, to the bricklayer, is a mixture of slaked lime, sand, and water which hardens slowly on drying. A little Portland cement may be added. The chemist knows that carbon dioxide of the air penetrates the wet mortar and reacts with the calcium hydroxide to form solid interlacing crystals of calcium carbonate, $\text{Ca(OH)}_2 + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O}$. The sand, preferably with sharp edges, merely gives bulk, rigidity, increases porosity, and reduces shrinkage. Yet even the chemist is surprised to learn that some mortar in Roman walls 2000 years old has not been completely carbonated. Evidently mere drying does not account for all of the solidity of mortar. Possibly the colloidal particles of calcium hydroxide "set" in some way suggestive of the drying of glue or water glass. Wall plaster differs from mortar only in containing hair as a binder. It is porous enough to allow considerable circulation of air through the walls. Usually it is surfaced with a paste of lime and gypsum.

Calcium Sulfate, CaSO_4 . The dihydrate of this salt, $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$, is found as gypsum in several states and is mined to the extent of a few million tons annually. It is heated a short time at 200° , causing the loss of three-fourths of its water, leaving the hemihydrate, $2 \text{CaSO}_4 \cdot \text{H}_2\text{O}$, or plaster of Paris. This residue, when mixed with the proper amount of water, sets to a white solid in from 5 to 15 minutes. What really happens is a reaction producing interlacing crystals of the dihydrate. The white finishing coat of common plastered walls contains plaster of Paris. Statuary is often made from it, because the material expands slightly on setting, thus taking a very sharp impression of the mold. Fragments have been found on ancient Greek temples. For commercial work, such as white plaster, stucco, and interior wall bricks, and wallboard, the setting process is retarded by the addition of glue or a product made by digesting hair with sodium hydroxide. By a recent process powdered gypsum heated with magnesium sulfate solution yields a plaster twice as strong.

Keene's cement, a hard finishing plaster, is prepared by heating gypsum, cooling, soaking in a solution of alum, and reheating.

Calcium Chloride, CaCl_2 . Most of the supply is obtained as a by-product in the (Solvay) ammonia soda process. The hexahydrate, $\text{CaCl}_2 \cdot 6 \text{H}_2\text{O}$, crystallizes from very concentrated solutions at ordinary temperatures.

As a drying agent anhydrous calcium chloride has its limitations. Ammonia cannot be dried over it because of the formation of $\text{CaCl}_2 \cdot 8 \text{NH}_3$. For a similar reason it is not suitable for the dehydration of alcohol. It finds a limited market as a dust layer, in coal washing, in tempering metals, and chiefly in forming a refrigerating brine for ice plants and cold-storage buildings.

Calcium Fluoride, CaF_2 . This salt occurs in nature as the mineral *fluorspar*. It melts at 1330° and is in demand as a slag former in metallurgy. Addition of calcium fluoride to some other salts lowers the melting point of the mixture. Glass and enamels are often made opaque with the addition of fluorspar. As a source of hydrofluoric acid it is already familiar to the student.

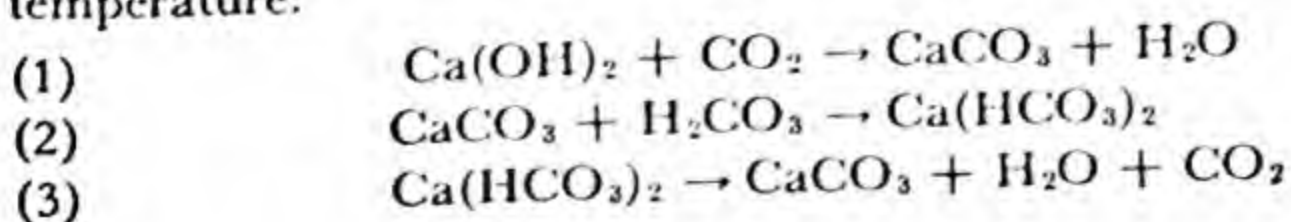
Calcium Cyanamide. High temperature reaction of calcium cyanamide, CaCN_2 , with carbon (and molten sodium chloride as a solvent) produces calcium cyanide, $\text{Ca}(\text{CN})_2$, useful in the mining industry, in the case-hardening of steel and as a source of hydrocyanic acid, HCN , in killing pests on citrus trees.

Calcium Hydride, CaH_2 . Calcium hydride reduces some refractory oxides such as TiO_2 and has some value as a reducing agent in organic chemistry.

Hardness of Water. Natural waters in contact with deposits of limestone or dolomite dissolve appreciable amounts of these rocks if carbon dioxide is present, as it always is. The soluble bicarbonates of calcium and magnesium formed give *temporary hardness* to the water, temporary because, on heating, these bicarbonates decompose with formation of the normal carbonates. Calcium carbonate may be precipitated.

Unless considerable evaporation has taken place, no natural water, on heating, yields enough magnesium carbonate to saturate the solution. Its solubility is 1 g. per liter.

Pass carbon dioxide into clear lime water. A precipitate of the carbonate forms. An excess of carbon dioxide dissolves this precipitate — the water has acquired temporary hardness. Now boil the solution and note the formation of insoluble calcium carbonate, not by evaporation but merely by raising the temperature.



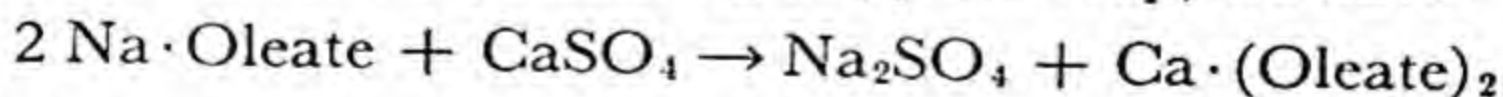
Permanent hardness is due largely to calcium and magnesium sulfates, which are not precipitated by mere boiling, unless the solution is made very concentrated by evaporation. A comparison of solubilities at ordinary temperatures is interesting.

Permanent hardness	{	1 liter of water dissolves	0.013 g. CaCO_3
		1 liter of water dissolves	1.000 g. MgCO_3
		1 liter of water dissolves	2.000 g. CaSO_4
		1 liter of water dissolves	354.000 g. MgSO_4

Hardness in commercial practice in this country is measured in grains per gallon or in parts per million, "p.p.m." of calcium carbonate. That is, one degree of hardness (United States) is 1 grain per gallon (0.017 gram per liter) or 17 p.p.m. Water with 50 p.p.m. is considered soft.

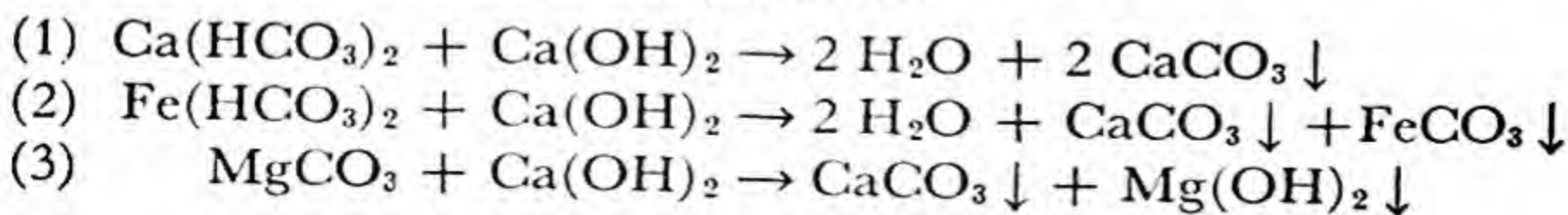
The Softening of Water. The importance of softening water is great. In boilers a hard scale of salts is left by the evaporation of feed water. This scale is a poor conductor of heat and causes a serious waste of fuel. A layer one-eighth inch thick causes a loss of 10–12 per cent of fuel. This loss increases as the square of the thickness. Furthermore superheating of the boiler may result. Cracking of the brittle scale may admit water to the overheated iron, causing an explosive generation of steam. If the temperature of the iron rises too high, a layer of the oxide, Fe_3O_4 , forms, weakening the boiler to the danger point.

Hardness of water causes an appalling waste of soap. No lather can form and consequently no cleansing be achieved until all the hardness has been precipitated at the expense of the soap. Thus, with sodium oleate, representing a typical soap, we have:

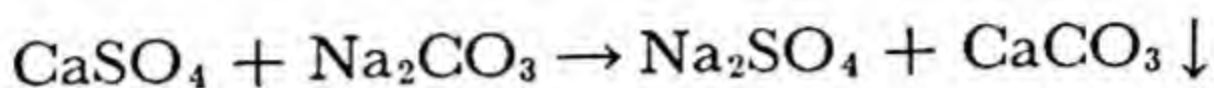


A further annoyance is caused by the stickiness of the calcium oleate formed. All calcium soaps are insoluble and curdy.

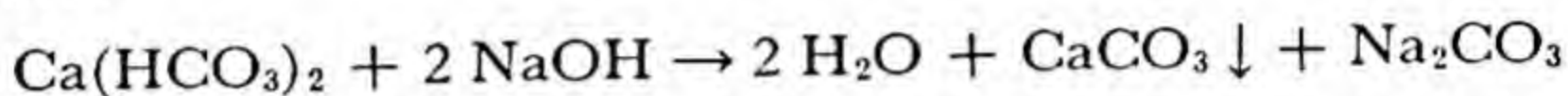
One of the cheapest softeners is lime itself. This sounds to the public like making matters worse, for it is often said that "lime causes the hardness of water." However, the following equations show the explanation of the paradox:



Reaction (3) is worthy of special attention. Either the bicarbonate or normal carbonate of magnesium is converted by any base into the decidedly insoluble hydroxide. Remember that one liter of water dissolves 1 g. of MgCO_3 but only 0.01 g. of Mg(OH)_2 . To precipitate permanent hardness crude "soda ash" is used:



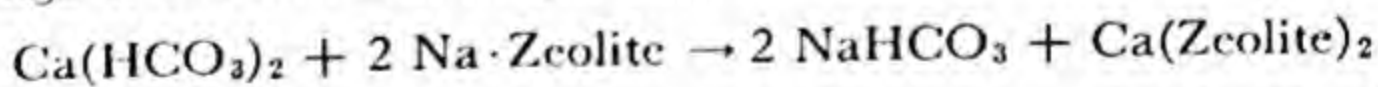
Sodium hydroxide is not as cheap, but it takes care of both kinds of hardness because the sodium carbonate produced in the following reaction reacts with the permanent hardness as indicated above:



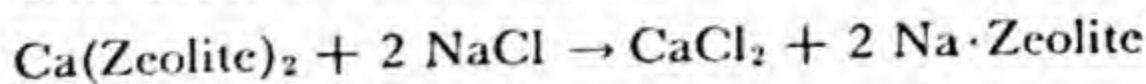
The common practice today is to use both lime and soda ash, varying the proportions with the seasonal variations in the water content. The limit of lime-soda softening is 50 p.p.m., which represents the combined solubilities of CaCO_3 and Mg(OH)_2 .

Sodium metaphosphate in the special form termed "hexameta-phosphate" recently has come into use as a water softener because it seems to form soluble complex compounds with calcium and magnesium (see page 380). When mixed with soap as a cleanser it prevents precipitation of curdy calcium and magnesium soaps.

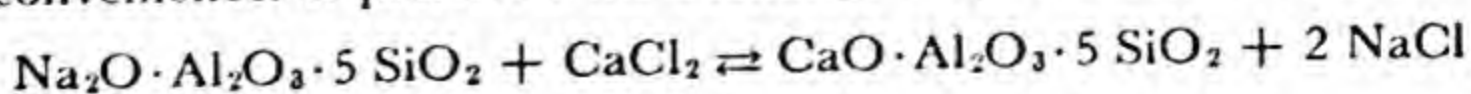
The modern *zeolite process* of softening yields water of zero degrees of hardness. No other chemical will do this in practice. An artificial zeolite (really a sodium silico-aluminate) is prepared and dried so as to retain its porous structure. When hard water slowly flows through a bed of this Na·Zeolite there is an exchange of calcium and magnesium for sodium.



After a time the zeolite no longer functions, having become Ca(Zeolite)_2 . Salt water (10 per cent) is then left on it for about an hour and, because the sodium chloride is now in excess, the Na·Zeolite is regenerated. After washing out the salt the Na·Zeolite is ready for use again:



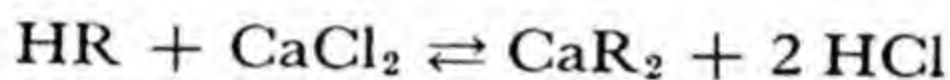
Of course there is absurdity in the use of "Zeolite" as a negative radical but it has convenience. If preferred the exchange may be written as below.



For a large area in California, water from the Colorado river (hardness, 300 p.p.m.) is limed to remove $\text{Ca}(\text{HCO}_3)_2$ and MgSO_4 . The CaSO_4 is then removed by the action of a zeolite.

A special zeolite, silver alumino-silicate, takes up Na^+ in exchange for its own Ag^+ which with Cl^- promptly forms a precipitate of silver chloride. Both ions are held in the mass, permitting filtration of salt-free water.

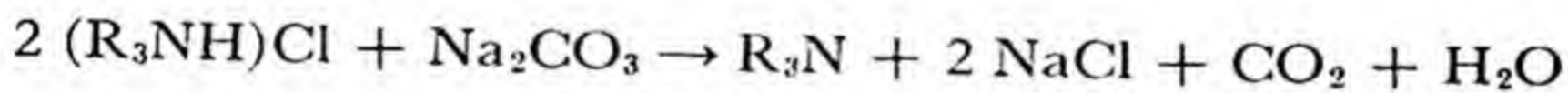
Cation Exchangers. Very effective phenolic resins are now on the market as base-exchange water softeners. Like the zeolites these cation exchangers remove Ca^{++} and Mg^{++} but they do it by giving H^+ to the water.



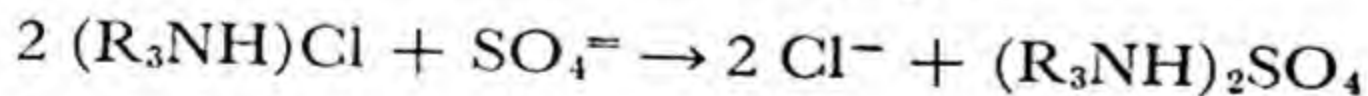
Regeneration is accomplished by washing CaR_2 with an excess of HCl or H_2SO_4 . Water passed through such resins may then be treated with "anion exchanger" resins to remove the entire acid molecule.

By use of cation exchangers valuable metals have been recovered from waste solutions.

Anion Exchangers. $\text{R}_3\text{N} + \text{HCl} \rightarrow (\text{R}_3\text{NH})\text{Cl}$. The exchange resin may then be regenerated by washing with a solution of sodium carbonate.



Such resins, sometimes called "anion exchangers," may be used to exchange Cl^- for $\text{SO}_4^{=}$, for example.

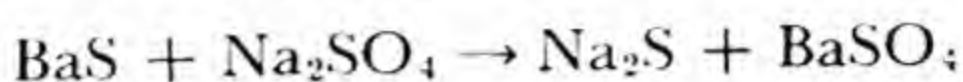


Tests for Calcium Compounds. The calcium flame is brick-red, but the precipitation of the extremely insoluble white calcium oxalate is usually taken as the best test for the presence of calcium.

BARIUM COMPOUNDS

Barium Sulfate, BaSO_4 . This mineral is the starting point for the preparation of nearly all barium compounds, including the precipitated form of barium sulfate. Coal mixed with barite is

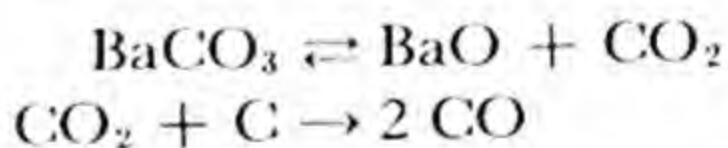
roasted four hours in a rotating furnace. The barium sulfide formed is treated with water. It is not very soluble, but is slowly hydrolyzed to the more soluble hydrosulfide. By reaction with "salt cake," Na_2SO_4 , the finely divided "blanc fixe" or precipitated barium sulfate is formed:



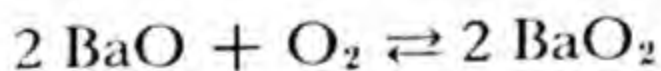
The sodium sulfide is a by-product necessary in making and using sulfur dyes. Blanc fixe is used, when pure white, as the body of lithograph inks and lake colors, and as filler for paints, rubber, linoleum, oilcloth, glazed paper, and plastics. Over 400,000 tons of ground rock barium sulfate are used annually in a heavy oil-drilling mud.

Other barium salts may be made by reaction of the sulfide with the proper compounds. When sodium carbonate is added to a solution of barium sulphate in fused sodium chloride barium carbonate is precipitated.

The Barium Oxides. The monoxide is generally made by roasting the carbonate with carbon which reduces the carbon dioxide formed to carbon monoxide. This lowers the partial pressure of the dioxide, sweeps it away, and thus facilitates decomposition of the carbonate:



Barium monoxide is an excellent dryer for gases when so prepared. The fused product is not as good. The monoxide is important mainly in preparing the dioxide by heating in air above 500° :



Barium peroxide (dioxide) is important as a source of hydrogen peroxide (see page 124). It acts on starch to form a "vegetable gluc."

Barium Hydroxide, $\text{Ba}(\text{OH})_2$. The hydroxide of barium is much more soluble than either calcium or strontium hydroxide. It is a moderately strong base and is used in quantitative analysis to absorb carbon dioxide.

Tests for Barium Compounds. The barium flame is green (distinctive except for copper and boric acid). The usual tests involve the precipitation of yellow barium chromate, and of white barium sulfate, insoluble in dilute acids.

STRONTIUM COMPOUNDS

The chief minerals of strontium, like those of calcium and barium, are the carbonate, SrCO_3 , and sulfate, SrSO_4 . Because of the brilliant flame color produced strontium compounds are used in fireworks and in tracer bullets.

Tests for Strontium Compounds. The characteristic carmine-red flame is an indication of strontium. Precipitation of its carbonate, sulfate, and oxalate, all white salts, aids in testing for the element. The peroxide is used in tracer bullets.

Calcium hydroxide is slightly soluble (lime water) and strontium hydroxide and barium hydroxide somewhat more so. The sulfate of barium is extremely insoluble (1 : 400,000), that of strontium is rather insoluble (1 : 8000), while calcium sulfate is slightly soluble (1 : 500). All the carbonates are insoluble, while the bicarbonates are soluble.

SOME COMPOUNDS OF MAGNESIUM

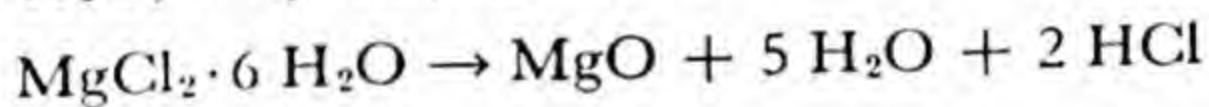
(The metal is discussed on page 531.)

FORMULA	NAME	SOLUBILITY	REMARKS
MgO	Magnesium oxide	Insoluble	White. Very high melting point. $\text{MgO} + \text{H}_2\text{O} \rightarrow \text{Mg(OH)}_2$
Mg(OH)_2	Magnesium hydroxide	Insoluble	White. Dissolves in NH_4Cl
$\text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$	Magnesium chloride	Very soluble	White. Is hydrolyzed, hot
MgCO_3	Magnesium carbonate	Insoluble	White. The basic carbonate is a heat insulator
$\text{MgSO}_4 \cdot 7 \text{H}_2\text{O}$	Magnesium sulfate (Epsom salts)	Soluble	White
$\text{Mg(ClO}_4)_2 \cdot 6 \text{H}_2\text{O}$	Magnesium perchlorate	Insoluble	White
$\text{MgNH}_4\text{PO}_4 \cdot 6 \text{H}_2\text{O}$	Magnesium ammonium phosphate	Insoluble	White

Magnesium Oxide, MgO . This white oxide is obtained by heating the carbonate to 350°C . ($\text{MgCO}_3 \rightarrow \text{MgO} + \text{CO}_2$). The reaction occurs at a lower temperature than that of a lime-kiln. Like calcium oxide, this oxide unites with water to form the hydroxide. Its chief use is as a refractory lining for high-temperature furnaces since it does not melt below 2800°C . If the carbonate is used as a lining (often mixed with oxides of iron and chromium), it is turned into the oxide during use by the heat of the furnace.

Magnesium Hydroxide, $\text{Mg}(\text{OH})_2$. This compound is white and rather insoluble, so a suspension of it in water is used medically to neutralize undue acidity of the stomach and as a laxative. As fast as the small amount in solution reacts with acid more solid dissolves, so a small and harmless concentration of OH^- ions is maintained until all the solid is dissolved. Magnesium hydroxide is soluble in solutions of ammonium chloride.

Magnesium Chloride, MgCl_2 . This salt is found in salt brines and is a by-product in separating potassium chloride from carnallite at Stassfurt. When heated sufficiently the crystallized salt, $\text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$, is hydrolyzed by its own water of crystallization:



This reaction shows the danger from the use of sea water in boilers. The acid released attacks the metal of the boiler. It would be possible to make all the hydrochloric acid we need by heating crystallized magnesium chloride. The anhydrous salt can be prepared by heating carefully the double salt $\text{MgCl}_2 \cdot \text{NH}_4\text{Cl} \cdot 6 \text{H}_2\text{O}$. The water is driven off first and then the ammonium chloride is volatilized. The crystallized salt is used as a filler for cotton and woolen goods and in making *magnesia cements*. A wet mixture of the oxide and chloride hardens with formation of the basic chloride. Sawdust, sand, or wood meal is added as a filler. Such compounds make wall plasters or floorings, or stucco for outside walls. Of course any filler may be added.

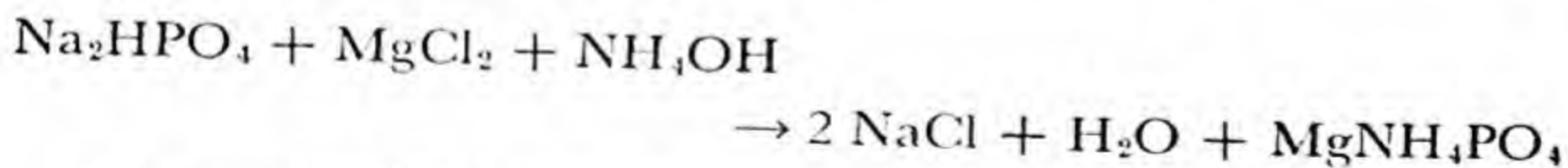
Magnesium Carbonate, MgCO_3 . This salt occurs as the mineral magnesite in Greece, Austria, the United States, and other countries. We use 200,000 tons yearly for lining open-hearth steel furnaces.

The normal carbonate cannot be obtained by precipitation with a solution of sodium carbonate. Instead, a basic salt is formed, its composition varying with the temperature and other conditions. The hydrolysis of sodium carbonate yields OH^- ions as well as $\text{CO}_3^{=}$ and, since magnesium hydroxide is even more insoluble than the carbonate, the conditions favor formation of a basic salt such as $3 \text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 3 \text{H}_2\text{O}$. This is sold as "magnesia alba" and used in cosmetics or in tooth powders. A crude product of loose fibrous structure is sold as "magnesia pipe covering" for heat insulation of steam pipes. In this field it is a rival of asbestos. It may be $\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 5 \text{H}_2\text{O}$.

Magnesium Sulfate, MgSO_4 . There are deposits of magnesium sulfate in the western states and at Stassfurt, Germany. When crystallized from solution at ordinary temperatures the heptahydrate, $\text{MgSO}_4 \cdot 7 \text{H}_2\text{O}$, is secured. This is sold as Epsom salts. The various hydrates lose water at 200° . Magnesium sulfate is used in dyeing, tanning, as a filler for cotton goods, and in medicine.

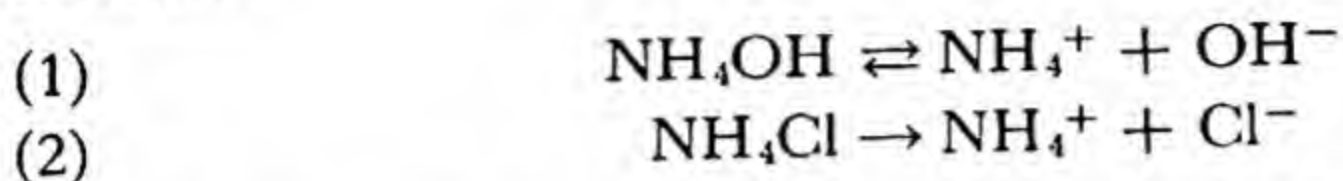
Asbestos. Asbestos fiber, $\text{CaMg}_3(\text{SiO}_3)_4$, occurs as a mineral in Canada and South Africa. It is valuable as a heat insulator, for auto brake linings and, when mixed with Portland cement, for asbestos shingles.

Magnesium Ammonium Phosphate, $\text{MgNH}_4\text{PO}_4 \cdot 6 \text{H}_2\text{O}$. When any soluble orthophosphate is added to a solution containing a magnesium salt, ammonium hydroxide and any ammonium salt a fine, crystalline precipitate of MgNH_4PO_4 is obtained. When ignited it forms the very stable pyrophosphate, $\text{Mg}_2\text{P}_2\text{O}_7$. This reaction is the basis of the quantitative determination of phosphates in fertilizers, etc.:

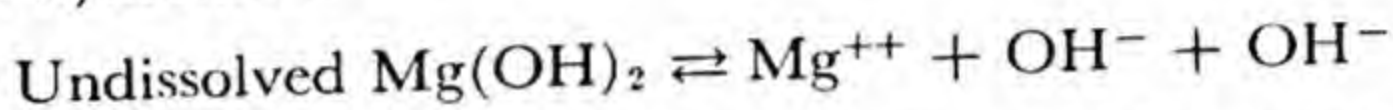


A reagent called *magnesia mixture* is used in this precipitation. It might seem impossible to prepare a solution containing both Mg^{++} ions and OH^- ions (from $\text{MgCl}_2 + \text{NH}_4\text{OH}$) and, in fact, if nothing else were added this mixture would form a precipitate of magnesium hydroxide. But the addition of any ammonium

salt prevents precipitation. Ammonium hydroxide is a weak base and its ionization is greatly suppressed by the mass action of a great excess of NH_4^+ ions from the well-ionized ammonium chloride:



The equilibrium in (1) is driven so far to the left that the concentration of OH^- ions left is very small, too small with the Mg^{++} ions present to exceed the solubility product of magnesium hydroxide. It is even possible to dissolve a precipitate of the hydroxide by the addition of an ammonium salt. It is evident that the following equilibrium must exist in a water suspension of magnesium hydroxide:



Removal of OH^- ions, whether by addition of H^+ ions from an acid or NH_4^+ ions from ammonium chloride, must disturb all equilibria to the right, with final solution of the precipitate.

Tests. The best test for magnesium compounds is the precipitation of the crystalline magnesium ammonium phosphate as described above.

BERYLLIUM AND RADIUM

Beryllium is divalent in its compounds. The insoluble white hydroxide, Be(OH)_2 is amphoteric, forming the strongly hydrolyzed BeCl_2 or beryllates such as Na_2BeO_2 or NaHBeO_2 . These salts, like the sulfate, are soluble.

Of *radium* salts only the soluble RaBr_2 and insoluble RaSO_4 are of interest.

Exercises

1. What are the uses of barium sulfate?
2. How does soap soften water? How do lime and soda soften water?
3. What happens to quicklime piled in the open air?
4. From what industry is calcium chloride a by-product?

450 COMPOUNDS OF ALKALINE EARTH METALS

5. If you had 22 kg. of barium sulfate how many kg. of barium peroxide could you make, assuming complete conversion? How proceed?
6. A sample of hard water is found to contain 85 parts per million of calcium bicarbonate. How much lime would be required to soften eight million liters of this water? Ignore other sources of hardness.
7. A sample of water contains 90 parts per million of magnesium bicarbonate. How much lime would be required to soften ten million liters of this water?
8. At 20° calcium hydroxide dissolves to the extent of 16.5 g. per liter. (a) What is the solubility in gram-molecules per liter? (b) If the base is completely ionized what will be the concentration of each ion in terms of gram ions per liter?
9. How could you make BaCO_3 from the mineral BaSO_4 ?
10. How could you make precipitated barium carbonate from the mineral, barium sulfate?
11. How can the exchange resins prepare almost pure water from ordinary hard water?
12. Could you obtain a magnesium salt from sea water by base exchange? Give details.

In the process of preparing metallic magnesium from sea water, containing a very low concentration of magnesium chloride, a suspension of calcium hydroxide is added. Equation?

Now what would happen if carbon dioxide were added to the products?

13. How can you mix Mg^{++} ions and OH^- ions in the same solution without getting the usual precipitate of $\text{Mg}(\text{OH})_2$?
14. What weight of magnesite will be required in the preparation of 563 g. of magnesium oxide?

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Chapter 39 COMPOUNDS OF COPPER, SILVER, AND GOLD

SOME COPPER COMPOUNDS

(The metal, 534, 573)

FORMULA	NAME	SOLUBILITY	REMARKS
Cu_2O	Cuprous oxide	Insoluble	Red
CuO	Cupric oxide	Insoluble	Black. From hydroxide, nitrate and carbonate
$\text{Cu}(\text{OH})_2$	Cupric hydroxide	Insoluble	Blue. Gelatinous
CuCl	Cuprous chloride	Sparingly soluble	White. From heated $\text{Cu} + \text{CuCl}_2$ solution in presence of HCl
$\text{CuCl}_2 \cdot 2 \text{H}_2\text{O}$	Cupric chloride	Soluble	Green
$\text{Cu}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$	Cupric nitrate	Soluble	Blue
CuS	Cupric sulfide	Very insoluble	Black. Attacked by warm HNO_3
$\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$	Cupric sulfate (blue vitriol)	Soluble	Blue. Chief copper salt
CuCN	Cuprous cyanide	Insoluble	Green. By spontaneous decomposition of $2 \text{Cu}(\text{CN})_2 \rightarrow 2 \text{CuCN} + (\text{CN})_2$
$\text{K}_2 \cdot \text{Cu}(\text{CN})_2$	Potassium cuprocyanide	Very soluble	Yellow-green. By excess KCN on CuCN
$\text{Cu}(\text{NH}_3)_4\text{SO}_4 \cdot \text{H}_2\text{O}$	Tetrammine cupric sulfate	Very soluble	Azure blue. By excess NH_4OH on CuSO_4 . Other similar copper compounds are known

Cuprous Oxide, Cu_2O . The simplest way to prepare this oxide is to reduce *Fehling's solution* with glucose. This famous solution is a mixture of copper sulfate, sodium hydroxide, and Rochelle salts (sodium potassium tartrate). A complex copper tartrate ion is formed which yields so few simple copper ions that no

cupric hydroxide is precipitated. The very small amount of cupric hydroxide in solution is reduced to the very insoluble cuprous oxide by added glucose. Since the occurrence of glucose in the urine is a symptom of diabetes, the use of Fehling's solution in diagnosis is important. Cuprous oxide has some use as a fungicide.

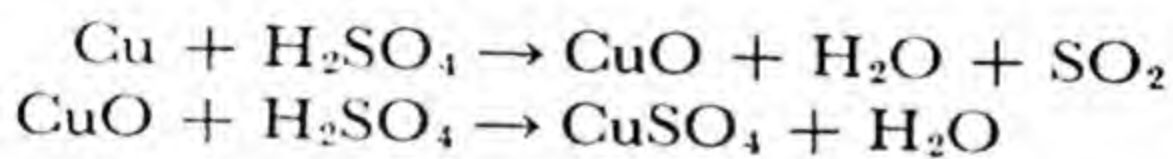
Cupric Oxide, CuO. This black oxide is prepared by igniting copper powder in the air, and by the ignition of the nitrate or carbonate.

Exercise

1. Why isn't a precipitate of cupric hydroxide formed in the reduction of Fehling's solution?

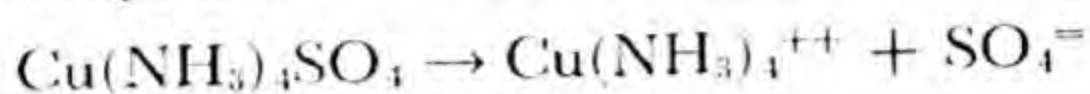
Cupric Sulfate, CuSO₄. This is the copper salt most used. It crystallizes in the triclinic system with five molecules of water as CuSO₄ · 5 H₂O. At 120°–140° it loses four molecules of water, but must be heated to 240° before it loses the fifth molecule of water. The anhydrous salt is white and when crystallized from hot concentrated sulfuric acid exhibits a different crystal form from the "blue vitriol." The anhydrous powder is sometimes used as a dryer for alcohol and such liquids. As it takes up water it turns blue. The term "vitriol" was once applied to any sulfate, and sulfuric acid was termed "oil of vitriol." Ferrous sulfate was green vitriol and zinc sulfate was white vitriol.

Cupric sulfate is made by the action of hot concentrated sulfuric acid on scrap copper:



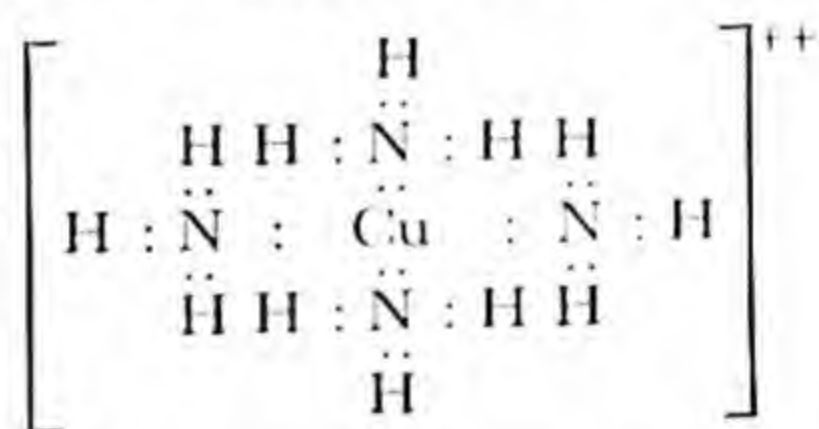
On a large scale it is produced by roasting natural sulfides and leaching them in the open air with water. Sometimes the copper ores are roasted and treated with sulfuric acid. Copper sulfate is used in calico printing, in electroplating, as a germicide, a fungicide, and as a source of other copper compounds. Bordeaux mixture, made from copper sulfate and calcium hydroxide, is much used as a fungicide spray on seeds, plants, and fruit.

Ammonia Compounds. Addition of ammonium hydroxide to a solution of copper sulfate, for example, first yields a green precipitate of basic cupric sulfate, $\text{Cu}_2(\text{OH})_2\text{SO}_4$, and with an excess of ammonium hydroxide forms the beautiful rich azure-blue solution of the complex ammono-cupric sulfate, $\text{Cu}(\text{NH}_3)_4\text{SO}_4 \cdot \text{H}_2\text{O}$. This very soluble salt can be precipitated by addition of alcohol. The soluble complex salt ionizes as follows:

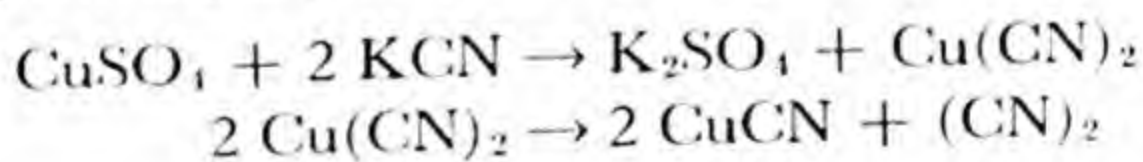


The $\text{Cu}(\text{NH}_3)_4^{++}$ ion yields such a low concentration of Cu^{++} ions that many slightly soluble copper compounds are dissolved by ammonium hydroxide. Even cupric hydroxide is dissolved by ammonium hydroxide, with the formation of $\text{Cu}(\text{NH}_3)_4(\text{OH})_2$. The soluble salts of copper form complex compounds as described for cupric sulfate. Cupric sulfide is one of the few copper compounds not forming a soluble complex with ammonia.

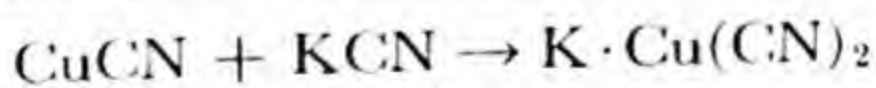
The cupric ion coordinates four NH_3 molecules in accord with its usual coordination number of four:



Complex Cyanides. Attempts to precipitate cupric cyanide fail. It decomposes spontaneously with escape of poisonous cyanogen gas, leaving a precipitate of cuprous cyanide:



With excess of potassium cyanide the insoluble cuprous cyanide dissolves, forming potassium cuprocyanide:



The complex negative $\text{Cu}(\text{CN})_2^-$ ion yields so few Cu^+ ions that all insoluble copper compounds are dissolved by alkali cyanides. Cupric sulfide is extremely insoluble. Its saturated solution

454 COMPOUNDS OF COPPER, SILVER, AND GOLD

(every precipitate settles from its own saturated solution) contains a minute concentration of Cu^{++} ions, but the complex cyanides of copper yield a still smaller concentration of Cu^{++} ions. Addition of potassium or sodium cyanide to cupric sulfide displaces every equilibrium in the direction favoring the existence of the lowest concentration of Cu^{++} ions. Consequently the sulfide dissolves. It is worth remembering that most simple cyanides, except those of the sodium group, are insoluble but that complex cyanides are soluble.

Tests for Copper Compounds. Copper compounds (after moistening with hydrochloric acid to form the volatile chloride) burn with a green flame. Precipitation of the red cupriferrrocyanide is a useful test. Usually the peculiar blue color developed when ammonium hydroxide is added to a solution of a copper compound is sufficient indication in analysis. Quantitatively the metal is frequently determined by electrolysis. The copper is plated on a weighed platinum cathode which is then dried, and weighed.

REACTIONS OF CUPRIC ION, Cu^{++}

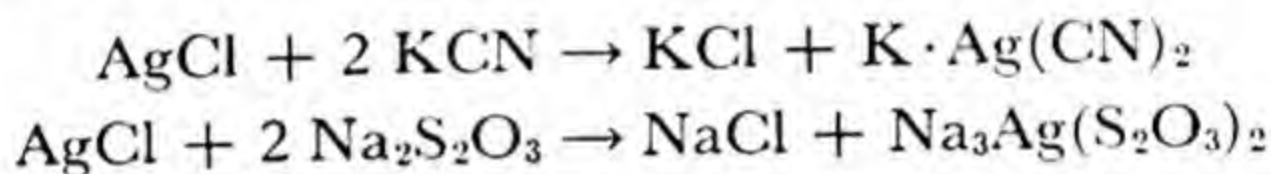
NaOH	$\text{Cu}^{++} + 2 \text{OH}^- \rightarrow \text{Cu}(\text{OH})_2$, blue
NH_4OH	$\text{Cu}^{++} + 4 \text{NH}_3 \rightarrow \text{Cu}(\text{NH}_3)_4^{++}$, azure blue
H_2S or Na_2S	$\text{Cu}^{++} + \text{S}^{--} \rightarrow \text{CuS}$, black
$\text{K}_4[\text{Fe}(\text{CN})_6]$	$2 \text{Cu}^{++} + [\text{Fe}(\text{CN})_6]^{4-} \rightarrow \text{Cu}_2[\text{Fe}(\text{CN})_6]$, red
KCN excess	$\text{C}_2\text{N}_2 + [\text{Cu}(\text{CN})_2]^-$, colorless
Zn	$\text{Cu}^{++} + \text{Zn} \rightarrow \text{Zn}^{++} + \text{Cu}$, reddish

SOME SILVER COMPOUNDS

FORMULA	NAME	SOLUBILITY	REMARKS
Ag_2O	Silver oxide	Slightly soluble	Brown. A strong base
AgCl	Silver chloride	Insoluble	White. Darkens in light
AgBr	Silver bromide	Insoluble	Yellow-white. Sensitive film of photography
AgI	Silver iodide	Very insoluble	Canary yellow
AgNO_3	Silver nitrate	Soluble	White. Chief silver salt
Ag_2SO_4	Silver sulfate	Slightly soluble	White
Ag_2CrO_4	Silver chromate	Insoluble	Red

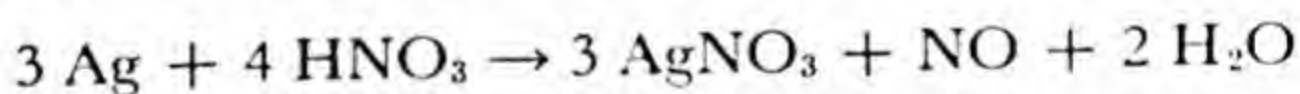
Silver Halides. These salts are usually formed by addition of a soluble halide to a solution of silver nitrate.

The chloride and bromide both change in the light, hence their use in photography. Silver iodide is not changed by light unless an excess of silver nitrate is present. The chloride is fairly soluble in concentrated hydrochloric acid, due to the formation of the complex acid HAgCl_2 . The AgCl_2^- ion yields a lower concentration of Ag^+ ions than is found in a saturated solution of silver chloride. The iodide does not dissolve in ammonium hydroxide because in its saturated solution the concentration of Ag^+ ions is less than that in a solution of the silver ammonia complex ion. With the less insoluble bromide and chloride the situation is different. The action of ammonium hydroxide on silver compounds is quite similar to its action on copper compounds. The same may be said for the solvent action of potassium cyanide. Sodium thiosulfate, "hypo," dissolves the silver halides because of the formation of a stable complex ion, $\text{Ag}(\text{S}_2\text{O}_3)_2^-$:



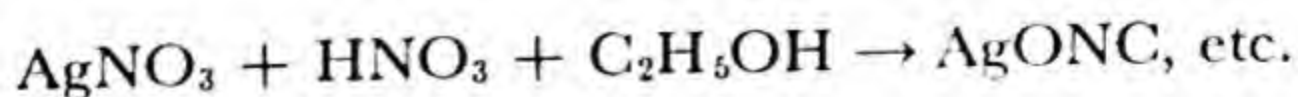
The use of silver halides in *Photography* is discussed on page 671.

Silver Nitrate. Silver is dissolved by nitric acid, an oxidizing acid, with formation of the nitrate, "lunar caustic":



Ammonium hydroxide is often added to silver nitrate solutions in order to secure the soluble complex ammonia compound for reduction to silver as in the making of mirrors. Only small quantities should be used, or if larger quantities are needed they should not be allowed to stand for long. Explosions of this mixture have occurred, probably due to the formation of an unstable nitrogen compound of silver.

Dangerous explosions have occurred when laboratory waste silver residues were washed with alcohol while traces of nitric acid were present. Apparently silver fulminate, AgONC , was formed.



2. How could you separate the silver from the copper in a silver coin?

Tests for Silver. The precipitation of white silver chloride, soluble in ammonium hydroxide without blackening, is usually considered a good test for silver compounds. Confirmatory tests may be obtained from the colors of the chromate and phosphate.

3. If silver and its compounds suddenly ceased to exist, could we find adequate substitutes?

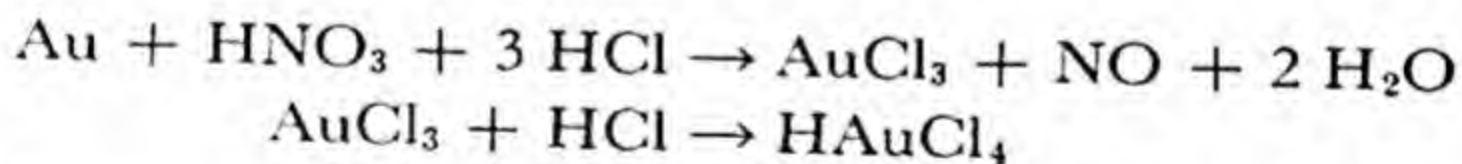
REACTIONS OF SILVER ION, Ag^+

HCl or KCl	$\text{Ag}^+ + \text{Cl}^- \rightarrow \text{AgCl}$, white
KBr	$\text{Ag}^+ + \text{Br}^- \rightarrow \text{AgBr}$, yellow-white
KI	$\text{Ag}^+ + \text{I}^- \rightarrow \text{AgI}$, yellow
NaOH	$2 \text{Ag}^+ + 2 \text{OH}^- \rightarrow \text{H}_2\text{O} + \text{Ag}_2\text{O}$, gray-brown
NH_4OH	$\text{Ag}^+ + 2 \text{NH}_3 \rightarrow [\text{Ag}(\text{NH}_3)_2]^+$, colorless
H_2S or Na_2S	$2 \text{Ag}^+ + \text{S}^{2-} \rightarrow \text{Ag}_2\text{S}$, black
Na_2CrO_4	$2 \text{Ag}^+ + \text{CrO}_4^{2-} \rightarrow \text{Ag}_2\text{CrO}_4$, red
Orthophosphates	$3 \text{Ag}^+ + \text{PO}_4^{3-} \rightarrow \text{Ag}_3\text{PO}_4$, yellow

GOLD COMPOUNDS

(The metal is discussed on page 524.)

Chemically, gold is inactive and resists the action of nitric acid yet free chlorine and bromine attack it. However, a mixture of concentrated nitric and hydrochloric acids (containing some nitrosyl chloride) called *aqua regia* dissolves gold, forming auric chloride, which, with excess of hydrochloric acid, forms chlorauric acid.



The sodium salt of this acid, $\text{NaAuCl}_4 \cdot 2 \text{H}_2\text{O}$, is used in photography as a toner.

Auric hydroxide, $\text{Au}(\text{OH})_3$, is amphoteric, and dissolves in potassium hydroxide to form potassium aurate, KAuO_2 .

Exercises

- Why does ammonia water fail to dissolve silver iodide while it does dissolve silver chloride?
- Review all the uses for sodium or potassium cyanide, both analytical and commercial.

6. Why can't we precipitate cupric sulfide from a solution containing considerable potassium cyanide mixed with copper salt?
7. What is a test for copper compounds?
8. Two grams of silver ore were dissolved in nitric acid and the silver present precipitated with hydrochloric acid. The resulting silver chloride weighed 1.576 g. Calculate the percentage of silver in the ore.
9. You need some "blue vitriol" and you have 644 g. of copper wire, and the usual laboratory reagents. How could you make the blue crystals desired, and how many grams could you make?

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Chapter 40 COMPOUNDS OF ZINC, CADMIUM, AND MERCURY

SOME COMPOUNDS OF ZINC

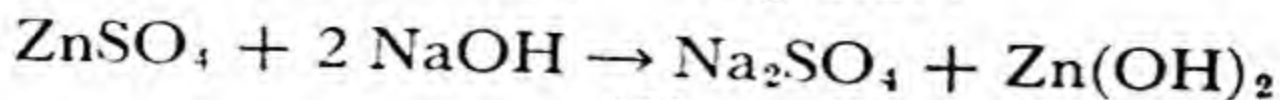
(The metal, 507, 536)

ZnO	Zinc oxide	Insoluble	White. Used in rubber, linoleum, etc.
Zn(OH) ₂	Zinc hydroxide	Insoluble	White. Amphoteric
Zn(ONa) ₂ · 4 H ₂ O	Sodium zincate	Soluble	Colorless
ZnCl ₂	Zinc chloride	Very soluble	White, Gelatinizes cellulose
ZnS	Zinc sulfide	Insoluble	White. Not as insoluble as CuS. Paint pigment

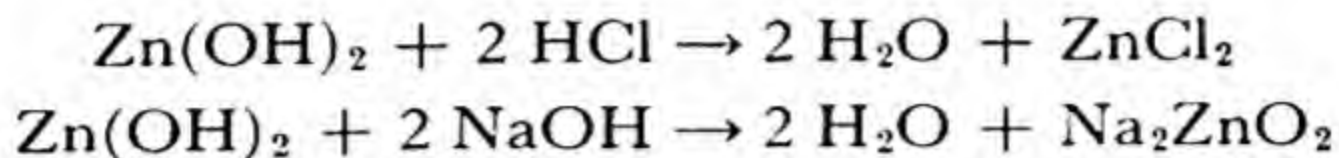
Zinc Oxide, ZnO. This white solid has been made by burning the metal (French process) but most of it is prepared by direct roasting of the ores (direct process) with a large excess of air. The dust is caught in bags which allow gases to go through. Ground with linsced oil, it forms one of the best white paints. Painters now prefer an addition of from 5 to 35 per cent basic lead sulfate to the zinc oxide in paints.

The greatest demand for zinc oxide, however, is as a filler in rubber goods, especially automobile tires. It is mixed with gutta percha and Venice turpentine to make surgeon's adhesive tape. As a filler in oilcloth, celluloid, and glazes it is important. Zinc oxide mixed with phosphoric acid sets quickly to a strong dental cement. Our annual production of this oxide is 115,000 tons.

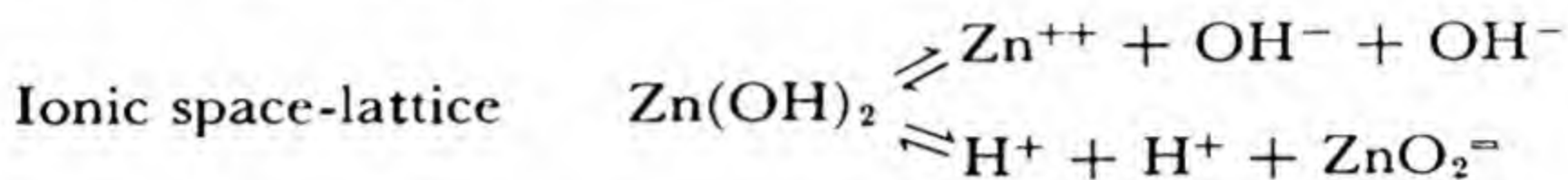
Zinc Hydroxide, Zn(OH)₂. This white insoluble compound is readily formed by union of the Zn⁺⁺ ion of any soluble zinc salt with the OH⁻ ions of any strong base:



It is an *amphoteric* hydroxide acting as an acid and a base. It is dissolved by a strong acid, which leads us to call it a base, but it is also dissolved by a strong base, so we are forced also to call it an acid:



Sodium zincate, $\text{Zn}(\text{ONa})_2$ or Na_2ZnO_2 , is a soluble salt. Zinc hydroxide evidently forms both H^+ ions and OH^- ions in water.



When an excess of H^+ ions (from a strong acid) is added, the OH^- ions are removed as water and every equilibrium is displaced in the direction of basic ionization. The entire precipitate is converted into zinc chloride or some such salt. On the other hand if an excess of OH^- ions is added (strong base), the H^+ ions will be removed and every equilibrium displaced in the direction of the acid ionization. All the precipitate is converted into some soluble salt, such as sodium zincate.

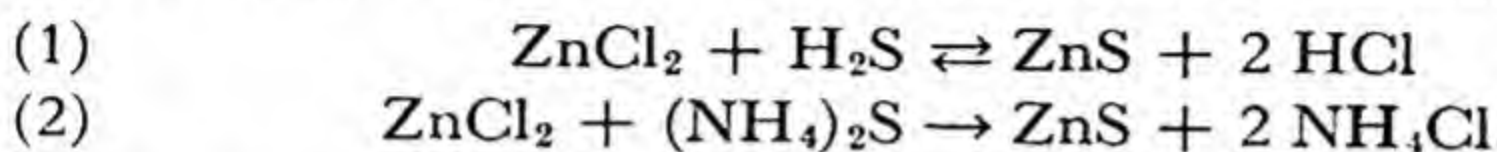
Zinc hydroxide also dissolves in an excess of ammonium hydroxide, not because of the formation of ammonium zincate (which would be completely hydrolyzed) but because of the formation of the soluble complex base, $\text{Zn}(\text{NH}_3)_4(\text{OH})_2$. The concentration of simple Zn^{++} ions derived from further ionization of the $\text{Zn}(\text{NH}_3)_4^{++}$ ion is lower than it is in a saturated solution of zinc hydroxide.

Exercise

1. If ammonium zincate could be formed in any way, how would it react in aqueous solution? Why?

A wet mixture of zinc chloride and zinc oxide sets to a solid cement of the basic chloride. In this respect zinc resembles magnesium.

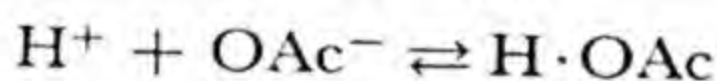
Zinc Sulfide, ZnS. As the mineral sphalerite, zinc sulfide is yellow to black, yielding a white streak, but the pure precipitated compound is white (the only white sulfide). In the laboratory precipitation is secured by union of Zn^{++} ions and $\text{S}^{=}$ ions. The sulfide ions may be from hydrogen sulfide or ammonium sulfide:



In reaction (1) there is a serious difficulty. At first the concentration of $\text{S}^{=}$ ions from the hydrogen sulfide may be sufficient, with the Zn^{++} ions, to exceed the solubility product of zinc sulfide.

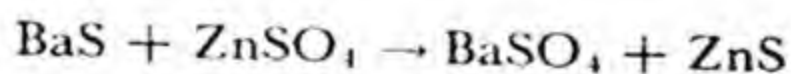
$$[\text{Zn}^{++}] \times [\text{S}^{=}] = K, \text{ solubility product}$$

But hydrochloric acid is formed as a by-product and its high concentration of H^{+} ions greatly represses the slight ionization of hydrogen sulfide. Consequently very soon the $\text{S}^{=}$ ion concentration falls so low that the solubility product of zinc sulfide is no longer exceeded and no further precipitation occurs. To be sure, addition of some other ion that would remove the offending H^{+} ions of the hydrochloric acid would permit precipitation. A strong base with its OH^{-} ions could do this. So could sodium acetate, with its acetate ions which tie up most of the H^{+} ions in the form of weakly ionized acetic acid:



Reaction (2) is favored because *salts* of hydrogen sulfide ionize freely and also because there is no acid formed to repress any essential ionization. So it is clear that zinc sulfide can be precipitated by passing hydrogen sulfide into a solution of any zinc salt containing sufficient sodium acetate or by the use of any soluble sulfide other than hydrogen sulfide.

Lithopone. This important pigment has been mentioned in connection with barium sulfide. It is made by mixing solutions of barium sulfide and zinc sulfate:



Both products are white and insoluble. The precipitate first formed has no body or hiding power, but when washed, dried, heated to dull redness, suddenly quenched in cold water, ground wet, washed, and dried again, it yields

an excellent pigment. Lithopone is a brilliant white with better hiding power than zinc oxide. It is unexcelled for interior painting, for first coats, linoleum, floor oilcloth, and rubber compounding.

Research has improved its quality so much that we now use over 160,000 tons of lithopone per year, for both outdoor and indoor paints, even in mixtures with white lead.

2. Why is zinc not used as a structural metal in the place of steel?

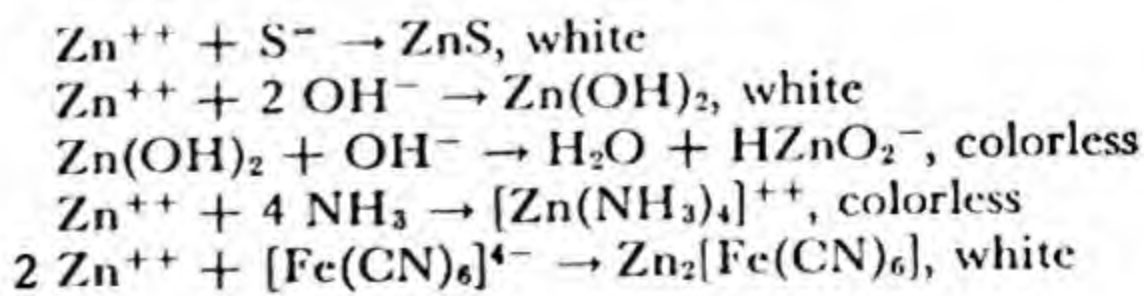
Tests. The characteristic white color of zinc sulfide precipitated from solutions of zinc salts or zincates by ammonium sulfide is a test for the metal. Any zinc compound moistened with a solution of cobalt nitrate and heated on charcoal gives a green stain (Rinmann's green).

ZINC CHART



REACTIONS OF ZINC ION, Zn^{++}

H_2S or $(NH_4)_2S$
 $NaOH$
 Excess $NaOH$
 NH_4OH
 $K_4[Fe(CN)_6]$



462 COMPOUNDS OF ZINC, CADMIUM, MERCURY

SOME CADMIUM COMPOUNDS

$\text{Cd}(\text{NO}_3)_2 \cdot 4 \text{H}_2\text{O}$	Cadmium nitrate	Soluble	White
CdS	Cadmium sulfide	Insoluble	Yellow. Good paint pigment. Not precipitated in very acid solution
$\text{K}_2\text{Cd}(\text{CN})_4$	Potassium cadmo-cyanide	Soluble	Colorless. Yields some Cd^{++} ions

Cadmium Sulfide, CdS . The most important compound of cadmium is cadmium sulfide. It is a very permanent bright yellow and is used as a pigment under the name "cadmium yellow." This sulfide is best precipitated in concentrations of HCl not exceeding 0.5 N.

Cadmium Chloride in solution exists as the complex $\text{Cd}[\text{CdCl}_4]$, a salt of the hypothetical acid, H_2CdCl_4 .

Cadmium-plated steel should not be used for food containers as toxic cadmium salts may be formed.

SOME COMPOUNDS OF MERCURY (MERCUROUS AND MERCURIC)

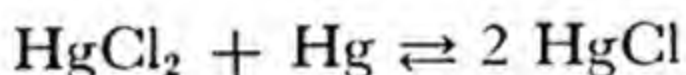
(The metal is discussed on page 537.)

FORMULA	NAME	SOLUBILITY	REMARKS
Hg_2O	Mercurous oxide	Insoluble	Black-brown
HgCl (or Hg_2Cl_2)	Mercurous chloride (calomel)	Insoluble	White. A medicine
$\text{HgNO}_3 \cdot \text{H}_2\text{O}$	Mercurous nitrate	Soluble	White. Readily hydrolyzed
Hg_2SO_4	Mercurous sulfate	Slightly soluble	White
HgO	Mercuric oxide	Insoluble	Red. Easily decomposed on heating
HgCl_2	Mercuric chloride (corrosive sublimate)	Somewhat soluble	White. Very poisonous
HgI_2	Mercuric iodide	Insoluble	Scarlet
$\text{K}_2 \cdot \text{HgI}_4$	Potassium mercuric iodide	Very soluble	Yellow. Complex salt
$\text{Hg}(\text{NO}_3)_2 \cdot \frac{1}{2} \text{H}_2\text{O}$	Mercuric nitrate	Very soluble	White
HgSO_4	Mercuric sulfate	Soluble	White
$\text{Hg}(\text{ONC})_2$	Mercuric fulminate	Insoluble	Detonator in explosive shells
HgS	Mercuric sulfide	Insoluble	Black. Dissolves in Na_2S
$\text{Hg}(\text{SNa})$	—	Soluble	Used in Group II, Qualitative Analysis

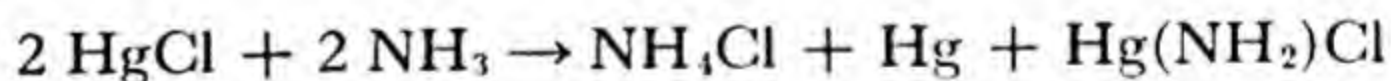
Tests. The yellow color of cadmium sulfide is a distinctive test for cadmium when separated from arsenic compounds. Cadmium differs from copper with which it is grouped in qualitative analysis in that the complex cadmicyanide $\text{K}_2\text{Cd}(\text{CN})_4$ yields enough Cd^{++} ions to allow precipitation of cadmium sulfide by hydrogen sulfide, while the complex cuprocyanide $\text{KCu}(\text{CN})_2$ does not yield enough Cu^+ ions to permit precipitation of insoluble copper sulfide.

MERCUROUS COMPOUNDS

Mercurous Chloride, HgCl . This insoluble white substance is used medicinally under the name *calomel*. It stimulates the liver and other glands. It is prepared by subliming mercury mixed with mercuric chloride:



This reaction is slightly reversible so the poisonous mercuric chloride must be washed out of the sublimate with alcohol or water. Medical men are careful to remember that light decomposes mercurous chloride ($2 \text{HgCl} \rightarrow \text{Hg} + \text{HgCl}_2$), forming some of the extremely poisonous mercuric chloride. Consequently they always keep calomel in dark bottles. The white chloride blackens in contact with ammonia. The color is due to the finely divided metal:



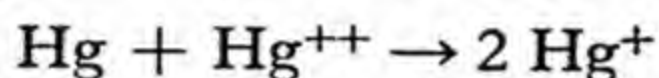
Probably the reaction should be written



The vapor corresponds to HgCl but the mercurous ion may be Hg_2^{++} as in Hg_2Cl_2 .

Mercurous Nitrate, $\text{HgNO}_3 \cdot \text{H}_2\text{O}$. This salt is obtained by the action of cold dilute nitric acid on excess mercury. Since mercury does not displace hydrogen from acids, the first step must be the formation of the oxide, which then reacts with the remaining nitric acid. Mercurous nitrate is hydrolyzed to such an extent that some nitric acid must be added to prevent precipitation of

the basic salt, $\text{Hg}_2(\text{OH})\text{NO}_3$. Some free mercury must also be present to reduce any mercuric ions formed by oxidation:



Mercurous Sulfate, Hg_2SO_4 . This white, slightly soluble salt is prepared in a manner analogous to that used for mercurous nitrate: an excess of mercury is treated with sulfuric acid. Its chief use is in the standard cells for electrical measurements.

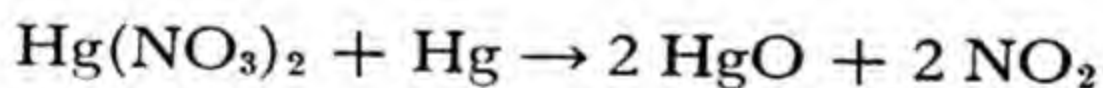
REACTIONS OF MERCUROUS ION, Hg^+

NaOH	$2 \text{Hg}^+ + 2 \text{OH}^- \rightarrow \text{Hg} + \text{HgO}$, black
NH_4OH	$\text{Hg}^+ + \text{NH}_4\text{OH} \rightarrow$ black precipitate
H_2S or Na_2S	$2 \text{Hg}^+ + \text{S}^{2-} \rightarrow \text{Hg} + \text{HgS}$, black
HCl	$\text{Hg}^+ + \text{Cl}^- \rightarrow \text{HgCl}$, white
KI	$\text{Hg}^+ + \text{I}^- \rightarrow \text{HgI}$, green-yellow

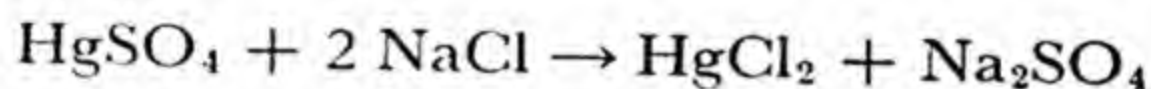
NOTE: Mercurous ion may be associated as Hg_2^{++} .

MERCURIC COMPOUNDS

Mercuric Oxide, HgO . Lavoisier made this red substance by heating mercury in air at 300° – 350° . This method is too slow, so usually it is prepared by heating dry mercuric nitrate with mercury:



Mercuric Chloride, HgCl_2 . Mercury unites with chlorine with a green flame and the production of mercuric chloride, but the usual method of preparation of mercuric chloride is to heat a mixture of mercuric sulfate and sodium chloride. A crystalline sublimate is secured:



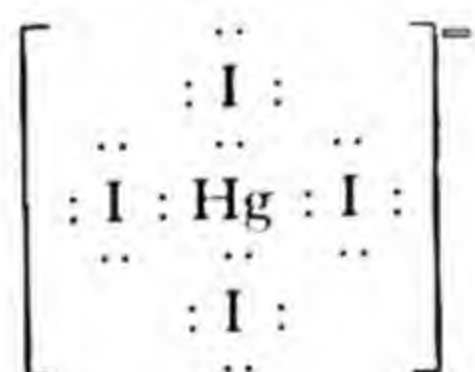
A little manganese dioxide may be added before subliming in order to oxidize any mercurous sulfate formed. The sublimate melts at 288° and boils at 303° . It is somewhat soluble in cold water but much more so in hot water. Mercuric chloride forms fairly soluble complex salts with sodium or potassium chloride, such as $\text{K}_2\text{HgCl}_4 \cdot \text{H}_2\text{O}$. The simple salt is very poorly ionized, differing from the nitrate. In 0.1 N solutions the chloride is only one per cent ionized and yields no precipitate with potassium

dichromate. On the other hand mercuric nitrate in 0.1 N solution is 10 per cent ionized and yields a precipitate with this reagent.

This salt is extremely poisonous and is known to the public as *corrosive sublimate*. Since it coagulates albumen, the white of egg is the proper antidote.

Mercuric Iodide, HgI_2 . Mercuric iodide is formed as a yellow precipitate, instantly changing to scarlet, when Hg^{++} ions and I^- ions are brought together. When heated above 126° the red modification turns yellow. On cooling below 126° the yellow tetragonal form may persist but on being scratched with some hard object it suddenly reverts to the red form. Similar color changes are found with some of the double iodides. With an excess of potassium iodide the soluble complex salt, $\text{K}_2 \cdot \text{HgI}_4$, is formed. Such a solution contains too low a concentration of simple Hg^{++} ions to yield a precipitate of the oxide on addition of potassium hydroxide. Such a mixture of the complex salt and alkali is known as Nessler's solution. It is especially useful in analysis to detect and determine ammonium compounds. With ammonia a yellow color or even a precipitate is formed.

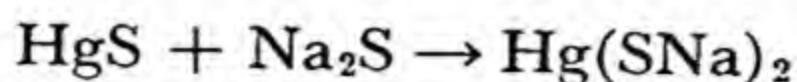
The HgI_4^- ion from $\text{K}_2 \cdot \text{HgI}_4$ may be diagrammed as follows:



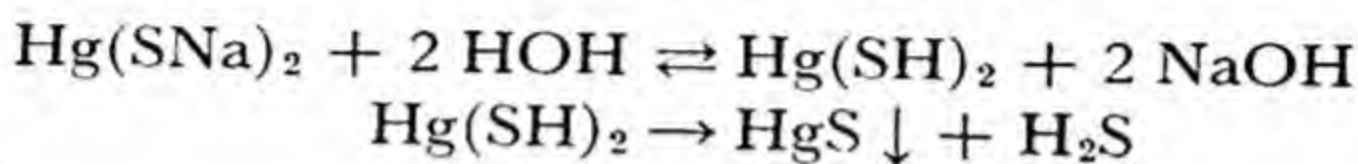
Reversible thermal color changes are useful in special paints applied to casings of bearings which may become overheated or as a stripe on boilers to indicate the water level. For example, the double or complex iodide $\text{Cu}_2(\text{HgI}_4)$ turns from scarlet to black rather sharply at 71° . For laboratory convenience marking sticks are obtainable for temperature readings from 125° to 700° in steps of 25° ; pellets reading 50° intervals up to 1600° .

Mercuric Nitrate, $\text{Hg}(\text{NO}_3)_2$. This is a colorless, soluble salt produced by completely dissolving mercury in an excess of hot nitric acid. (Compare with mercurous nitrate.) Its solution is very acid because of hydrolysis.

Mercuric Sulfate, HgSO_4 . By heating mercury in concentrated sulfuric acid *mercuric sulfate* is formed. *Mercuric sulfide* is very insoluble, yet it is dissolved by a solution of sodium sulfide:

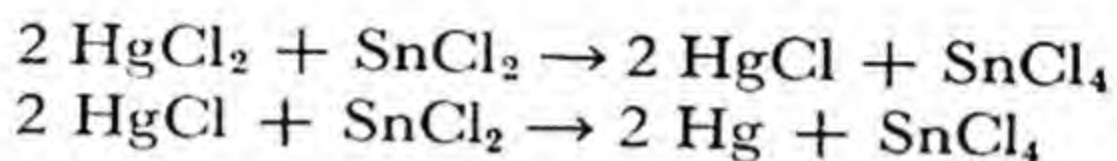


This soluble sodium salt of the unstable and weak thio acid, $\text{Hg}(\text{SH})_2$, is hydrolyzed with formation of the free acid, which decomposes at once into a precipitate of HgS , and H_2S , unless an excess of NaOH is added to repress hydrolysis:



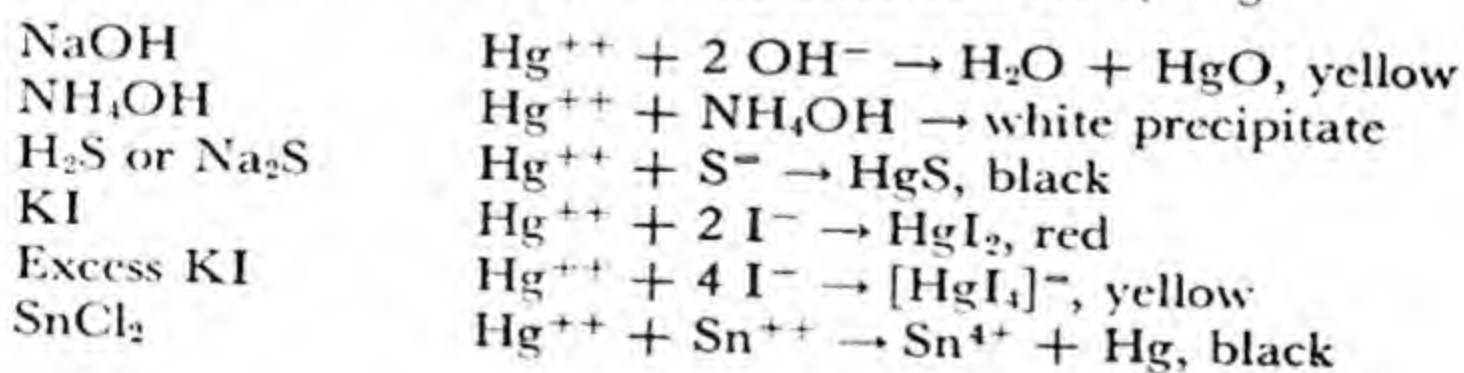
Tests. Precipitation of white mercurous chloride which turns black with ammonia is the usual test for mercurous salts.

Mercuric salts are detected by formation of the black sulfide, which is then converted into mercuric chloride by aqua regia and reduced by stannous chloride:



At first the white calomel is precipitated and later this is completely reduced to the black, finely-divided mercury.

REACTIONS OF MERCURIC ION, Hg^{++}



Exercises

- How much mercury and sulfur dioxide can be obtained from 8 metric tons of cinnabar ore (60 per cent pure HgS)?
- How does the mercury boiler work?
- At 400° the vapor density of mercurous chloride indicates a decomposition into two molecules. We might assume that



6. A man bought 250 g. of mercuric chloride, but received, by mistake, mercurous chloride. Being a chemist, he converted it into mercuric chloride. How much mercuric chloride did he gain by the mistake?
7. Why doesn't hydrogen sulfide precipitate all the Zn^{++} from a solution of zinc chloride?

References

- Blank, E. W., "Reversible Chromatic Thermosensitivity." *J. Chem. Education*, 20, 171 (1943).
- Hanley, H. R., "Story of Zinc." *J. Chem. Education*, 10, 600, 682 (1933).

Chapter 41 COMPOUNDS OF ALUMINUM

ALUMINUM CHART

(The metal is discussed on pages 520 and 539.)

FORMULA	NAME	SOLUBILITY	REMARKS
Al_2O_3	Aluminum oxide	Insoluble	White. The ruby is Al_2O_3 with trace of chromium
$\text{Al}(\text{OH})_3$	Aluminum hydroxide	Insoluble	White. Amphoteric
$\text{AlCl}_3 \cdot 6 \text{H}_2\text{O}$	Aluminum chloride	Soluble	White
AlCl_3	Aluminum chloride (anhydrous)	Reacts with H_2O	Yellow-white. Important catalyst
$\text{Al}_2(\text{SO}_4)_3$	Aluminum sulfate	Soluble	White. Used in water treatment, etc.
$\text{KAl}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$	Common alum	Soluble	White. Readily purified by recrystallization
$\text{KCr}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$	Chrome alum	Soluble	Violet
NaAlO_2	Sodium aluminate	Soluble	Colorless. Intermediate in purification of bauxite ore
$3 \text{CaO} \cdot \text{Al}_2\text{O}_3$	Tricalcium aluminate	Insoluble	White. A component of Portland cement

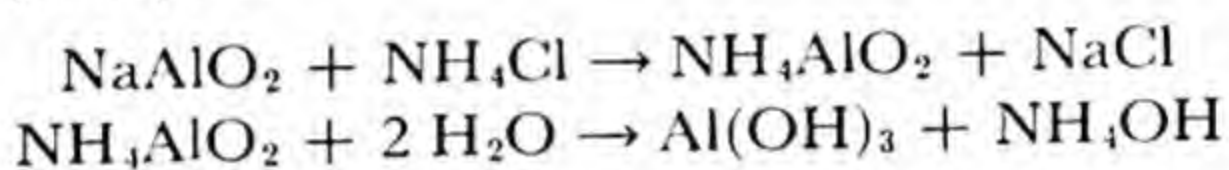
Aluminum Oxide, Al_2O_3 . The mineral bauxite may be considered as the hydrated oxide. Corundum is an impure form of the oxide, extremely hard, hence the variety known as emery is used as an abrasive or polishing material. If the mineral bauxite is heated until portions fuse (about 2050°) and then ground to a

powder, corundum is obtained and is used on a large scale as an abrasive under the name alundum.

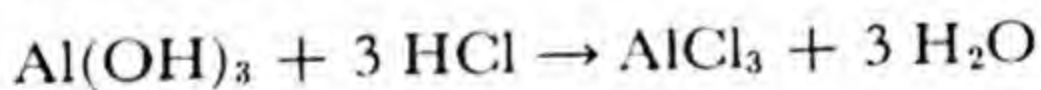
The gems ruby and sapphire are crystals of pure corundum colored by traces of other metallic oxides. Synthetic rubies are made very successfully by heating ammonium alum and a trace of chrome alum in the oxy-hydrogen flame. We now are making millions of synthetic sapphires as jewel bearings for instruments on planes and naval vessels, as spray nozzles and as thread-guides in textile spinning.

Aluminum Hydroxide, $\text{Al}(\text{OH})_3$. This white, insoluble hydroxide or hydrous oxide is precipitated when any soluble base is added to a solution of an aluminum salt; in other words, by the arrangement in a space lattice of Al^{+++} ions with OH^- ions.

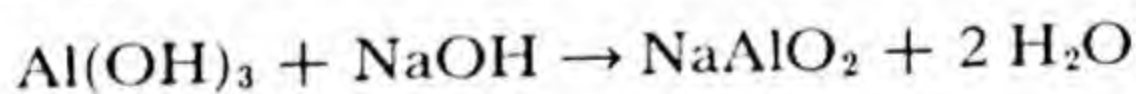
Although aluminum hydroxide is a very weak base it is even weaker as an acid, consequently ammonium aluminate is completely hydrolyzed:



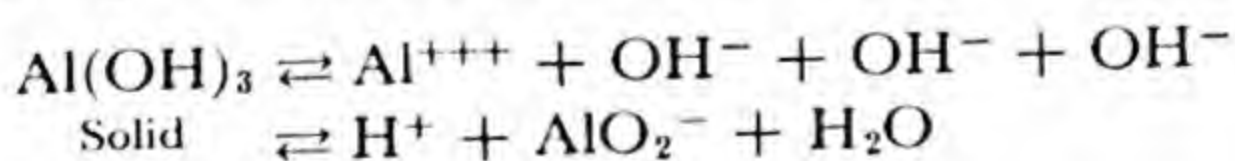
That it is a basic hydroxide is clearly shown by the fact that many acids dissolve it:



That it is an acid is just as clearly shown by the startling fact that sodium and potassium hydroxides dissolve it:



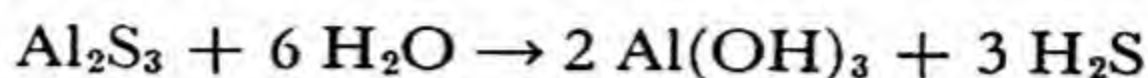
There is but one explanation. Aluminum hydroxide is amphoteric, ionizing as an acid and as a base:



These equilibria may be disturbed in one direction by the addition of an excess of OH^- ions or in another direction by the addition of an excess of H^+ ions. (Compare with zinc hydroxide.)

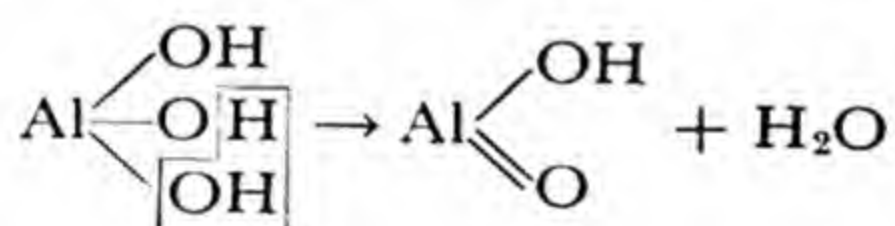
With very weak bases or very weak acids, aluminum hydroxide forms no salts. For instance, the carbonates and sulfides of many

metals are precipitated from solution, but these salts of aluminum are not so precipitated. If aluminum sulfide, Al_2S_3 , is formed by direct union of the heated elements and then added to water, it is completely hydrolyzed, with precipitation of the hydroxide:

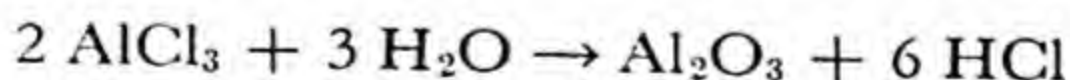


In fact, any attempt to precipitate aluminum sulfide by adding ammonium sulfide to a solution of an aluminum salt results only in precipitation of the hydroxide. Furthermore a solution of ammonium sulfide contains a noticeable concentration of hydroxyl ions.

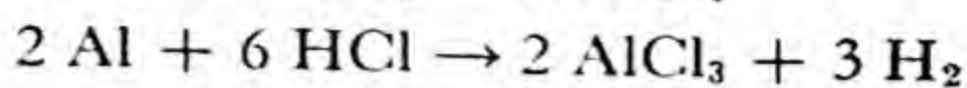
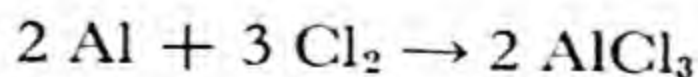
When it acts as an acid, aluminum hydroxide is called aluminic acid, H_3AlO_3 , and its salts aluminates. By loss of water metaluminic acid, HAlO_2 , may form. The most stable aluminates at high temperatures are the salts of the meta-acid, such as NaAlO_2 :



Aluminum Chloride, AlCl_3 . When aluminum or its hydroxide is dissolved in hydrochloric acid and the solution concentrated, crystals of the chloride, $\text{AlCl}_3 \cdot 6 \text{H}_2\text{O}$, are formed. Any attempt to secure the useful anhydrous salt by driving off the water fails. With rise in temperature hydrolysis increases, so that only the oxide and hydrochloric acid are formed:

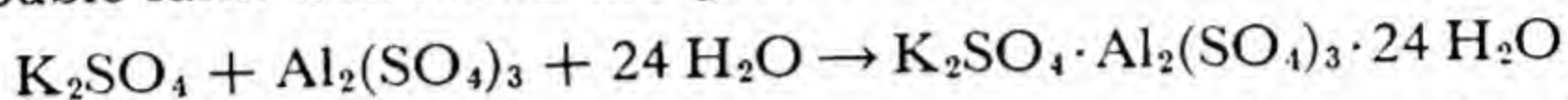


This reaction is really reversible and the water could be removed safely in a stream of dry hydrogen chloride. By mass action this would push the equilibrium to the left and yet remove the water. In actual practice it is simpler to leave water out of the situation. Dry chlorine, or even hydrogen chloride not quite dry, is passed through a tube containing hot aluminum. Aluminum chloride sublimes:

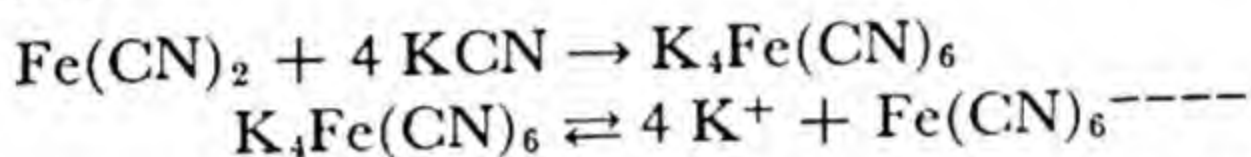


Crude anhydrous AlCl_3 is formed by the joint attack of hot carbon and chlorine on the oxide (from bauxite), the other product being carbon monoxide. The anhydrous salt is very useful in some organic reactions and in oil refining. It fumes strongly in moist air, due to hydrolysis.

Double Salts. When certain salts are mixed in proper proportions and the solution concentrated slowly, crystals appear containing both salts in a very definite proportion. These are called double salts. The alums are good examples:

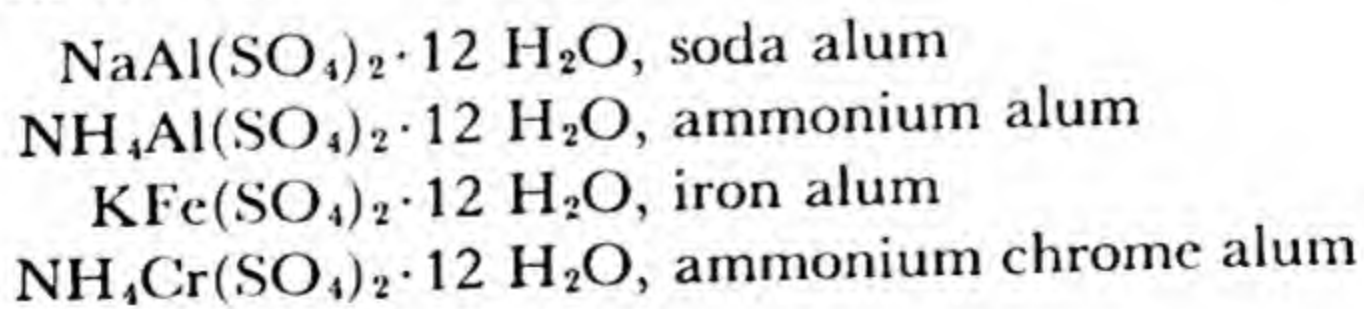


In dilute solution these double salts yield the simple ions of their constituent salts. However, some salts on mixing form compounds which do not yield all the simple ions again. These are called *complex salts*:



The potassium ferrocyanide mentioned here yields no simple iron ions, but instead the complex ferrocyanide ion. As we have seen, a similar complex ion of cadmicyanide breaks down to a slight extent, yielding some simple cadmium ions, but at equilibrium much of the complex still remains.

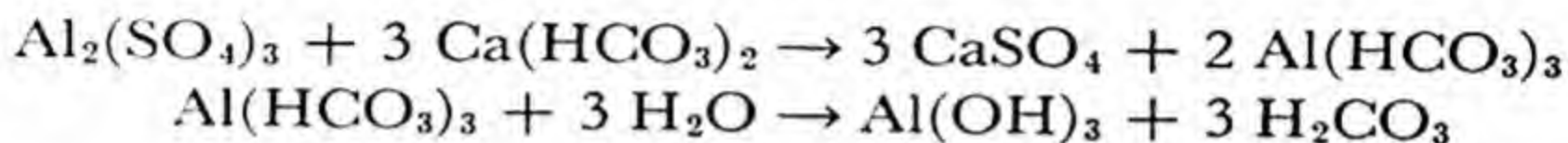
The Alums. Common alum, $\text{KAl}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$, may be formed as above by merely mixing solutions of potassium sulfate and aluminum sulfate in molecular proportions. On concentration the solution yields octahedral crystals. Because many substituted alums are possible by replacing potassium with almost any monovalent metal (Na, Cs, Rb, Ag, NH_4), this is sometimes distinguished as "potash alum." Still further substitution is possible, in that any one of several trivalent metals may be used in place of aluminum. These all crystallize with twelve molecules of water and all have the same characteristic crystalline form. Below are given some of the best known alums:



Exercise

1. Why isn't the double sulfate formed by mixing solutions of ferrous sulfate, FeSO_4 , and ammonium sulfate, $(\text{NH}_4)_2\text{SO}_4$, an alum?

Common alum has many uses, but for most of these the cheaper aluminum sulfate is just as good. The alums have one advantage for certain special uses—they crystallize better than the simple sulfate and consequently are more readily purified by fractional crystallization. The plain sulfate is added to city water supplies to aid in removing suspended matter and bacteria. If the water is soft, a little lime is added at the same time to insure precipitation of the gelatinous aluminum hydroxide. The bicarbonates of hard water serve as well as the lime:



In sizing paper to prevent the spread of ink it is the practice to mix an alkaline rosin soap and aluminum sulfate in the pulp. The resulting reaction yields free rosin throughout the paper where it is wanted. On passing through hot rolls the rosin melts throughout the paper.

Aluminum sulfate is used to the extent of 325,000 tons a year, and this is augmented by 18,000 tons of sodium aluminum sulfate.

A number of aluminum salts are used as mordants, substances which fix a dye to the fiber.

Brick and Pottery. Kaolin or china clay is the weathered residue from feldspar. Its composition is represented by $\text{H}_2\text{Al}_2(\text{SiO}_4)_2 \cdot \text{H}_2\text{O}$, or by $\text{Al}_2\text{O}_3 \cdot 2 \text{SiO}_2 \cdot 2 \text{H}_2\text{O}$, while that of feldspar, its ancestor, is KAlSi_3O_8 . Common clay owes its color to impurities, usually oxides of iron. In burning brick or tile the impurities fuse and act as a bond for the clay particles. Fire brick, with its great infusibility, must be made from very pure clay. It softens at about 1500°C .

The kaolin type of clay (china clay used in ceramics) has little affinity for water, does not swell much when wet, and has very little base exchange property. The montmorillonite type (the other extreme) absorbs much water, swells markedly when wet,

and has high base exchange action. Other clays (the illitic type) are intermediate.

Sand-lime brick is hydrated calcium silicate, formed by the action of steam on a mixture of lime and fine silicon dioxide.

Porcelain is a fired mixture of kaolin and feldspar. The more fusible feldspar binds the kaolin particles and makes the mass translucent. When such ware is dipped into a water suspension of ground feldspar, dried, and burned again, it receives a glaze of feldspar. Cheaper ware as ordinary table dishes may be so porous that a glaze is absolutely essential. If the glaze has a different coefficient of expansion from the body of the ware, it cracks with temperature changes.

Portland Cement. The Romans ground together volcanic ashes and lime to form a cement that, when mixed with water, set to a solid. Some specimens of this Puzzolan cement are still

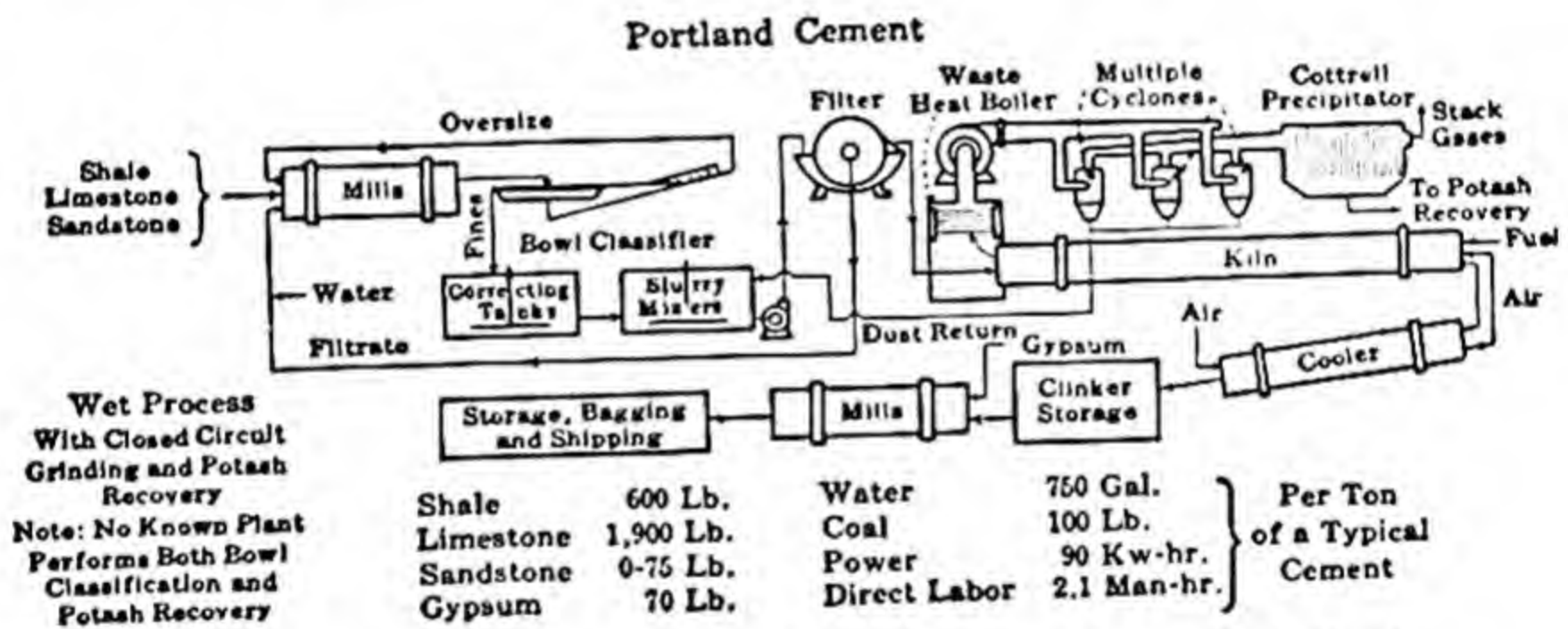


Fig. 133. Portland cement flowsheet. (Courtesy Chem. Met. Eng.)

in good condition. Today we do practically the same thing in grinding together blast-furnace slag (granulated) and lime. But the best of these hydraulic cements is the modern Portland cement. The essential raw materials are clay and limestone. The raw materials are finely ground, fired in a rotary kiln to incipient fusion (the edges of lumps just melting), and the clinkered product is ground again. These rotary kilns are nearly horizontal, from 60 to 200 feet long, and 6 to 9 feet in diameter. They are heated with powdered coal (see copper smelting). Nearly 8,000,000 tons of powdered coal are used as fuel in the cement

industry, annually. The cement powder (of 200-mesh fineness) when used for walls, walks, etc., is mixed wet with sand and gravel as a filler to form *concrete*. One part of cement is added to 4 parts of sand and 8 of gravel. The surfacing mixture contains one part cement to 2 or 3 of sand. The United States has produced as much as 187,000,000 barrels of cement in a single year.

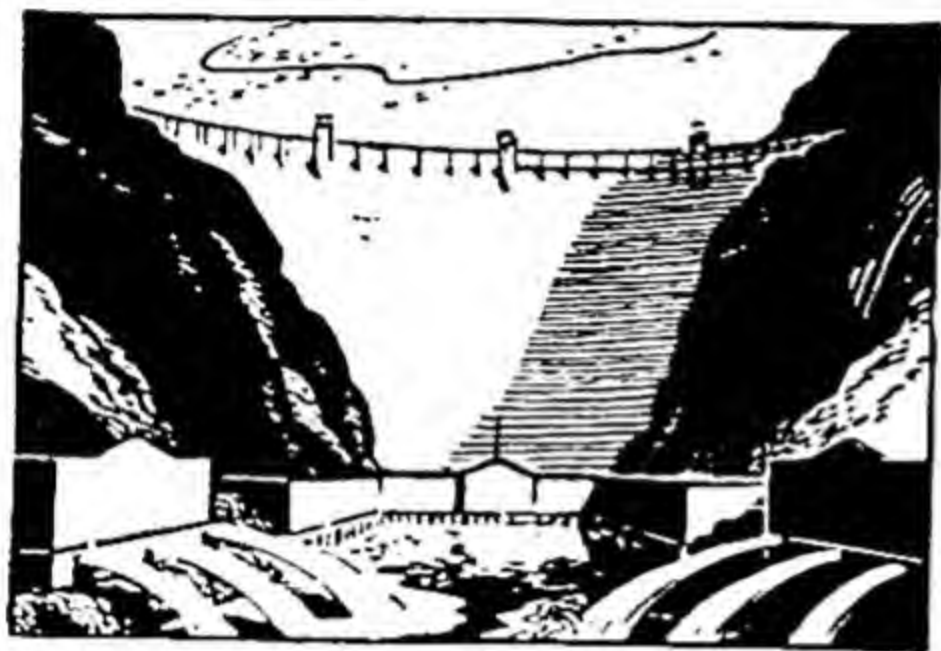


Fig. 134. Boulder Dam would have been impossible without Portland cement.

A cement road requires a week or more for "setting," in fact it is all the better if the surface is covered with a layer of wet straw while it cures.

The Boulder Dam would not have been built but for the discovery of the Portland cement process. This mammoth structure, containing 4,400,000 cubic yards of concrete, developed so

much heat from the setting reactions that it was necessary to incorporate 750 miles of cooling pipe as the mass grew in height. Cold water was circulated through the pipes but finally they were filled with concrete paste. Without this precaution temperatures above normal would have continued for two centuries, it was estimated, and dangerous shrinkage cracks would have developed.

Portland cement is, within limits:

- 3 $\text{CaO} \cdot \text{SiO}_2$, slow to set
- 2 $\text{CaO} \cdot \text{SiO}_2$, slowest, complete in months
- 3 $\text{CaO} \cdot \text{Al}_2\text{O}_3$, quick-setting
- 4 $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$, maximum strength in 1 day

Gypsum, not above 4 per cent, is added to retard the set or hardening. Setting results from the hydration, hydrolysis, and crystallization of components after addition of the proper amount of water. The electron microscope shows the presence of a fibrous mass and spheres of calcium hydroxide; of rhombic slabs of hydrated dicalcium silicate; of hexagonal plates and needles of

hydrated tricalcium aluminate; and needles of a complex calcium sulfoaluminate.

Soil water containing calcium sulfate, or other sulfates, causes swelling and disintegration of cement due to a change of the tricalcium silicate to calcium sulfoaluminate. Too much alkali in soil also damages cement.

The Rare Earths. Monozite sand, a mixture of complex phosphates of the rare earths occurs in Brazil and Ceylon. The valence number of these elements in their compounds is three like M_2O_3 . However, cerium ores form a dioxide, CeO_2 . The old gas mantle was essentially a mixture of 1 per cent cerium dioxide and 99 per cent of thorium dioxide. A pyrophoric alloy of rare earth metals is used as the friction gas lighter. Thorium has now become very important because, like Uranium-235, it is fissionable, may yield atomic power.

The rare earths have a number of minor uses such as in the cores of carbons for searchlights and movie studio lights, in making glass for certain optical purposes, and in some enamels.

Indium forms an amphoteric hydroxide, $In(OH)_3$. **Thallium** forms $Tl(OH)_3$ which reacts with acids (but not with bases) to form salts such as $TlCl_3$, strongly hydrolyzed. Another hydroxide, $TlOH$ is a strong base, moderately soluble in water. **Gallium** hydroxide, $Ga(OH)_3$, is amphoteric.

Exercises

2. What is an alum? Name some.
3. Define a double salt; a complex salt. Name some complex mercury salts.
4. How much aluminum may be obtained from 1 metric ton (1000 kg.) of an ore which is 85 per cent bauxite, $Al_2O_3 \cdot 2 H_2O$?
5. A certain sample of bauxite contained 13 per cent iron oxide and 87 per cent $Al_2O_3 \cdot 3 H_2O$. How many grams of the ore would be required to produce 1750 g. of aluminum?
6. What weight of aluminum oxide can be obtained from 412 g. of sodium aluminate ($NaAlO_2$)? How?
7. If water, Portland cement, sand, soda, and granular aluminum were mixed, what might happen? Can you see any uses for which the final product might have advantages?

8. What is clay? If heated with concentrated sulfuric acid, new products are formed. What are they? How could you hope to make metallic aluminum from any of these products? In what locations might such a process have the best chance of success?
9. Since iron and steel corrode or rust in contact with water, oxygen, and carbonic acid of the air, would you have reason to hope that the steel rods or beams in "reinforced concrete" would not rust? Why?
10. Add a solution of $(\text{NH}_4)_2\text{S}$ to a solution of AlCl_3 . What is the precipitate?
11. If told that a certain white powder is zinc sulfate or magnesium hydroxide or aluminum hydroxide, how would you test for each?
12. The heat of combustion of calcium is greater (per gram equivalent) than the heat of combustion of aluminum. Could you reduce CaO to metallic calcium by the thermit process?

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Chapter 42 COMPOUNDS OF TIN AND LEAD

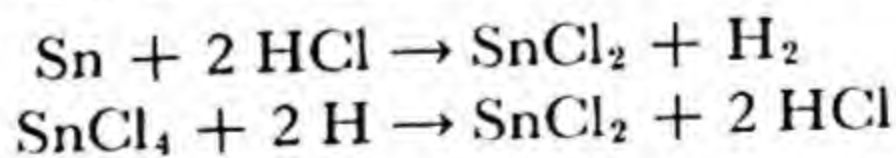
SOME COMPOUNDS OF TIN

(The metal, 508, 543)

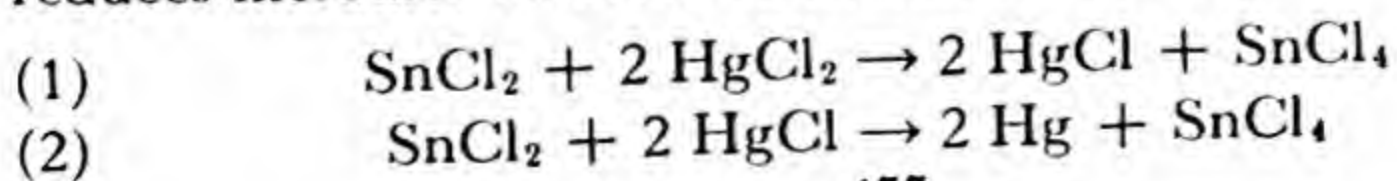
FORMULA	NAME	SOLUBILITY	REMARKS
SnO	Stannous oxide	Insoluble	Black
Sn(OH) ₂	Stannous hydroxide	Insoluble	White. Amphoteric
Sn(ONa) ₂	Sodium stannite	Soluble	Colorless
SnCl ₂ · 2 H ₂ O	Stannous chloride	Soluble	White
SnS	Stannous sulfide	Insoluble	Brown-black. Soluble in polysulfides
SnO ₂	Stannic oxide	Insoluble	Cassiterite ore
(H ₂ SnO ₃) ₂	Metastannic acid	Insoluble	Converted to soluble stannate by fusion with NaOH
Na ₂ SnO ₃	Sodium stannate	Soluble	
SnCl ₄	Stannic chloride	Reacts with H ₂ O	Colorless liquid. Fumes in moist air
SnS ₂	Stannic sulfide	Insoluble	Yellow
Na ₂ SnS ₃	Sodium sulfostannate	Soluble	By reaction of SnS + Na ₂ S ₂

STANNOUS COMPOUNDS

Stannous Chloride, SnCl₂. When tin is dissolved in acids the hydrogen evolved insures the formation of salts of the lower valence number. The same is true of iron and other metals which exhibit two valence numbers. If any stannic chloride were formed, it would be reduced by the active hydrogen:



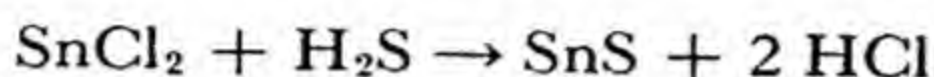
In solution this salt is a good reducing agent. For example, it reduces mercuric chloride to metallic mercury:



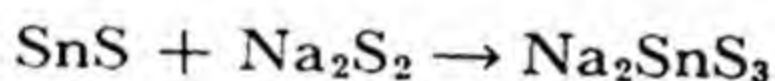
Stannous Hydroxide. White, gelatinous hydroxide, $\text{Sn}(\text{OH})_2$, stannous hydroxide, is much like zinc hydroxide and aluminum hydroxide in that it dissolves in strong acids as well as in strong bases. Therefore it is amphoteric.

The soluble salt, $\text{Sn}(\text{ONa})_2$ or Na_2SnO_2 , is called sodium stannite, which suggests that stannous hydroxide may also be termed *stannous acid*.

Stannous Sulfide, SnS . This insoluble brown-black sulfide is precipitated by hydrogen sulfide from solutions of stannous salts:

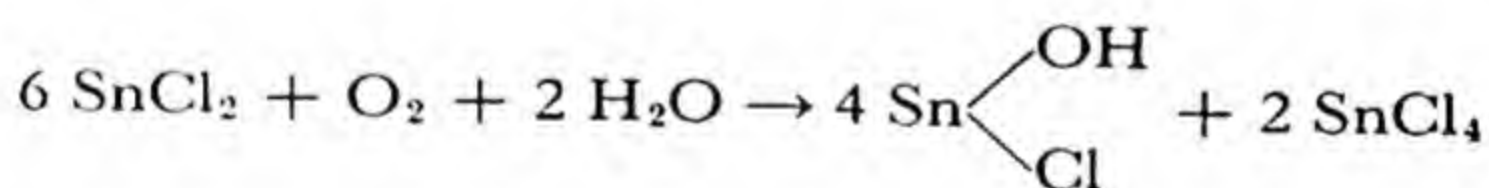


As this reaction shows, it is not dissolved by dilute acids. Unlike the lower sulfides of arsenic and antimony, it is not soluble in the simple alkali sulfides. With polysulfides it forms the soluble sulfostannates which are important in qualitative analysis:

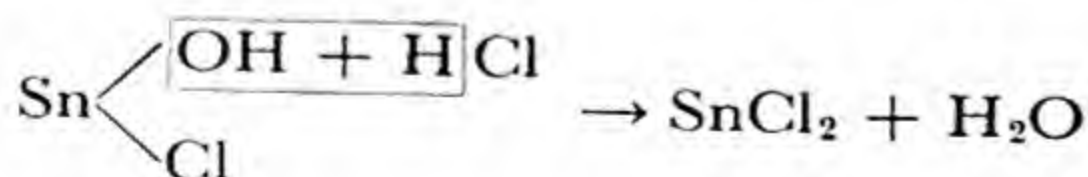


STANNIC COMPOUNDS

A solution of stannous chloride is partially oxidized in air with the formation of stannic chloride and the basic chloride of stannous tin:



By addition of acid this basic chloride is converted into stannous chloride:



An easy way to keep a solution of a stannous salt is to have a few pieces of metallic tin and some acid present. The metal acts as a reducing agent, as does the hydrogen released.

Stannic Chloride, SnCl_4 . Stannic chloride is prepared in solution by passing chlorine into a solution of stannous chloride:



The liquid anhydrous form is made by passing chlorine over hot tin.

Exercise

1. If you added bromine water to a solution of stannous chloride, how would you know when all the tin was oxidized? Write the equation.

α -Stannic Acid, H_2SnO_3 . The alpha form of stannic acid is readily prepared by addition of ammonium hydroxide or sodium hydroxide to a solution of a stannic salt. We might expect $\text{Sn}(\text{OH})_4$, but this loses water and yields H_2SnO_3 . The rest of the water may be driven off and the anhydride, SnO_2 , secured. The white gelatinous precipitate of α -stannic acid dissolves readily in excess alkali, forming stannates, such as Na_2SnO_3 . The acid also dissolves easily in dilute mineral acids.

β -Stannic Acid (H_2SnO_3)₈ (Metastannic Acid). When slightly diluted nitric acid reacts with tin, a hydrated form of the dioxide is produced as a white, insoluble powder. This form of stannic acid, unlike the alpha, is almost insoluble in dilute mineral acids. It is not readily attacked by alkalies, but if fused with sodium hydroxide it is converted into sodium α -stannate, identical with the salt secured by using the simple dioxide.

When metastannic acid is ignited ordinary tin oxide, SnO_2 , results. It is an important constituent of white enamels.

Tests. Tin compounds are usually recognized by converting them into stannous chloride which reduces mercuric chloride to white, insoluble mercurous chloride and gray finely divided mercury (see page 466). The brown-black stannous sulfide, soluble in polysulfides, and the yellow stannic sulfide, soluble in alkali sulfides, are both well known in analysis. The ease of reduction of the oxide by hot carbon is noteworthy.

2. Why are we able to make sulfuric acid in lead chambers without loss of lead?
3. How does the existence of lead carbonate in water suspension show that $\text{Pb}(\text{OH})_2$ is not an extremely weak base?

SOME COMPOUNDS OF LEAD

(The metal is discussed on pages 517 and 544.)

FORMULA	NAME	SOLUBILITY	REMARKS
PbO	Lead monoxide (litharge)	Insoluble	Yellow. Anhydride of Pb(OH) ₂
PbO ₂	Lead dioxide	Insoluble	Brown. Anhydride of Pb(OH) ₄
Pb ₃ O ₄	Red lead	Insoluble	Red. Probably 2 PbO. PbO ₂ . Pigment
PbCl ₂	Lead chloride	Insoluble but soluble hot	White
PbI ₂	Lead iodide	Insoluble but soluble hot	Yellow
PbS	Lead sulfide	Insoluble	Black
Pb(NO ₃) ₂	Lead nitrate	Soluble	White
Pb(C ₂ H ₃ O ₂) ₂ · 3 H ₂ O	Lead acetate (sugar of lead)	Soluble	White. Poisonous, like all soluble lead salts
PbSO ₄	Lead sulfate	Insoluble	White
PbCrO ₄	Lead chromate	Insoluble	Yellow
2 PbCO ₃ · Pb(OH) ₂	White lead	Insoluble	White. Paint pigment
Pb(OH) ₂	Plumbous acid	Insoluble	Amphoteric

Oxides. There are four oxides of lead, although only two are in common use:

PbO, lead monoxide (litharge), yellow red

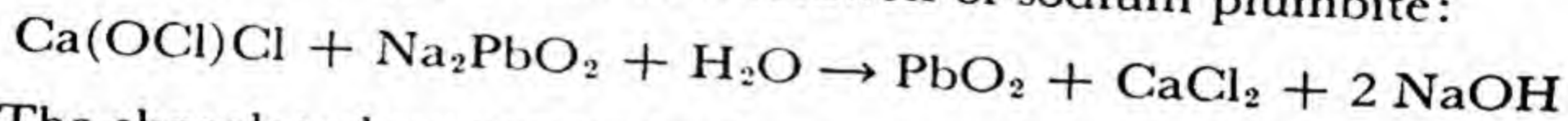
Pb₂O₃, lead trioxide, orange yellow

PbO₂, lead dioxide, chocolate brown

Pb₃O₄, lead tetroxide (minium or red lead), red

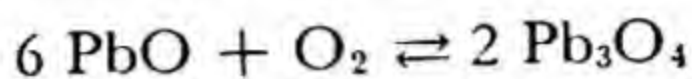
Lead Monoxide (Litharge), PbO. This yellow-red powder is obtained by heating lead in the air. Above 585° all lead oxides pass into the monoxide. It is used in glazing pottery, making glass (of the cut-glass type), and is a starting point in preparing other lead compounds.

Lead Dioxide, PbO₂. The simplest method of preparation is to add bleaching powder to a solution of sodium plumbite:



The chocolate-brown powder is a powerful oxidizing agent. Hydrogen sulfide gas passed over it is ignited. It may be considered the anhydride of plumbic acid (or hydroxide), Pb(OH)₄.

Red Lead, Pb_3O_4 . Red lead, or minium, is prepared (40,000 tons annually in the United States) by carefully heating litharge, PbO , in air not above 585° . Above that temperature it decomposes into the monoxide and oxygen.



It is used in considerable quantities as a pigment in red paints and also as an oxidizing agent. Writing the formula as $2 \text{PbO} \cdot \text{PbO}_2$ we can understand why nitric acid dissolves only the basic PbO , leaving the acidic PbO_2 . As a paint pigment red lead forms tough, elastic lead soaps.

The Lead Storage Battery. This important cell is described on page 578 under Electrochemistry.

The Halides of Lead. Lead chloride, PbCl_2 , formed by the union of Pb^{++} ions and Cl^- ions or by the action of hot concentrated hydrochloric acid on the monoxide or carbonate, is somewhat soluble in hot water, but only sparingly soluble at room temperatures. On cooling the hot-water solution white crystals separate. It is much more spectacular to cool a hot-water solution of the yellow lead iodide, PbI_2 . Beautiful gleaming gold crystals settle like so many spangles. The bromide is much like the chloride and iodide in solubility. All these halides of lead form complex salts with the alkali halides (compare with mercuric halides).

White Lead Paint. A paint is prepared by grinding some heavy insoluble *pigment* of sufficient covering power with linseed oil or other drying oils. Finally thinners are added. The drying of paint is not really a loss of water, but oxidation of the oil with the formation of a tough, solid film. This oxidation of the oil is hastened by catalytic dryers made by boiling manganese dioxide, etc., with linseed oil. Among the pigments used are white lead, red lead, barium sulfate, lead chromate, zinc oxide, cadmium sulfide, lithopone, iron oxides, and TiO_2 , but the one most used is *white lead* or basic lead carbonate, $\text{Pb}(\text{OH})_2 \cdot 2 \text{PbCO}_3$, known to the ancient Greeks. In the United States alone nearly 200,000 tons are used annually.

By the famous *Old Dutch process*, lead sheets rolled into "buckles" are placed in earthenware pots just above some dilute acetic acid. A layer of these

pots is set on spent tan bark from the tannery, another layer of pots is supported by loose boards above the first, then a layer of tan bark, and so on until a chamber $20 \times 20 \times 30$ feet is filled. Fermentation of the tan bark yields carbon dioxide and heat, up to 85°C . The heat vaporizes acetic acid and moisture, which attack the lead with the formation of basic lead acetate. The carbon dioxide changes this into basic lead carbonate. After three or four months the sealed chamber is opened. The corroded buckles are rolled, washed, and screened by means of silk cloth containing 30,000 openings to the square inch. The fine white powder is ground in oil and marketed.

By the *Carter quick process* lead powder is sprayed with acetic acid in the presence of carbon dioxide. This is a one-day process.

In the *Sperry electrolytic process* lead ions go into solution from anodes, meet acetate and carbonate ions in the bath and form a precipitate of "white lead." Explain.

Emulsions of alkyd resins are beginning to rival paints for coating metals.

Exercises

4. What is formed when tin is treated with hydrochloric acid? With nitric acid, dilute and concentrated?
5. How is litharge made? Red lead? "White lead"?

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Chapter 43 COMPOUNDS OF THE CHROMIUM GROUP AND MANGANESE

Chromium and Manganese

Although chromium is found in Group VI of the Periodic Table and manganese in Group VII, they have so many points in common that they should be studied together. These two elements are remarkable for the number of their oxidation stages and the great variety of their compounds. Their lower oxides are basic and their higher oxides acidic (compare with lead).

SOME COMPOUNDS OF CHROMIUM

(The metal is discussed on pages 509 and 547.)

FORMULA	NAME	SOLUBILITY	REMARKS	
CrCl_2	Chromous chloride	Soluble	Product of Cr + HCl Valence	2
$\text{CrCl}_3 \cdot 6 \text{H}_2\text{O}$	Chromic chloride	Soluble	Green	3
Cr_2O_3	Chromium trioxide	Insoluble	Green	3
CrO_3	Chromic anhydride	Reacts with H_2O	Red. Anhydride of H_2CrO_4	6
$\text{Cr}(\text{OH})_3$	Chromic hydroxide	Insoluble	Blue-green	3
H_2CrO_4	Chromic acid	Soluble	Yellow	6
K_2CrO_4	Potassium chromate	Soluble	Yellow	6
$\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2 \text{H}_2\text{O}$	Sodium dichromate	Soluble	Orange	6
PbCrO_4	Lead chromate	Insoluble	Yellow. Pigment	6
BaCrO_4	Barium chromate	Insoluble	Yellow. Pigment	6
Ag_2CrO_4	Silver chromate	Insoluble	Red. Pigment	6

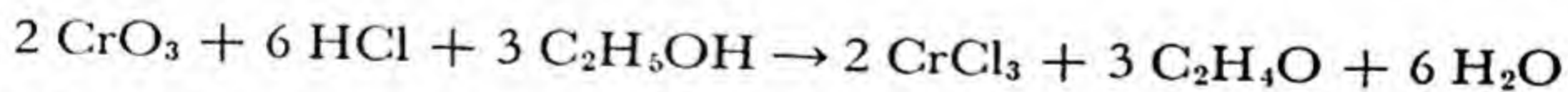
Such salts as $K_2Cr_2O_7$, potassium dichromate, may be written, $K_2O \cdot 2 CrO_3$, somewhat like the salts of pyrosulfuric acid. The chromate, K_2CrO_4 , could be written $K_2O \cdot CrO_3$. In $K_2Cr_2O_7$, the oxide of chromium is the same as in K_2CrO_4 . Therefore, no new valence series is illustrated, but a new set of chromates, just as there are two sets of phosphates, ortho and meta, and two sets of sulfates derived from the ortho and pyro acids.

There are, therefore, three principal series of salts of chromium — chromous, chromic, and the chromates. Of these, the chromous salts are so easily oxidized to the chromic forms that they are preserved with difficulty.

The normal electron arrangement in the chromium atom, counting electron shells from the nucleus out, is 2, 8, 8, 6 as in the chromates and dichromates. Here the valence shell contains six electrons. In the green and violet chromic salts the arrangement is 2, 8, 11, 3 and the valence shell contains only three electrons.

Chromous Compounds. When chromium is dissolved in hydrochloric acid it is *chromous chloride*, $CrCl_2$, not chromic chloride, $CrCl_3$, that is secured. The active hydrogen released and the excess metal would reduce any chromic chloride to the lower form.

Chromic Compounds. The ordinary form of chromic chloride is soluble and green. It is made easily by reduction of a dichromate or of CrO_3 , chromic anhydride, with alcohol, C_2H_5OH , in a solution of hydrochloric acid:

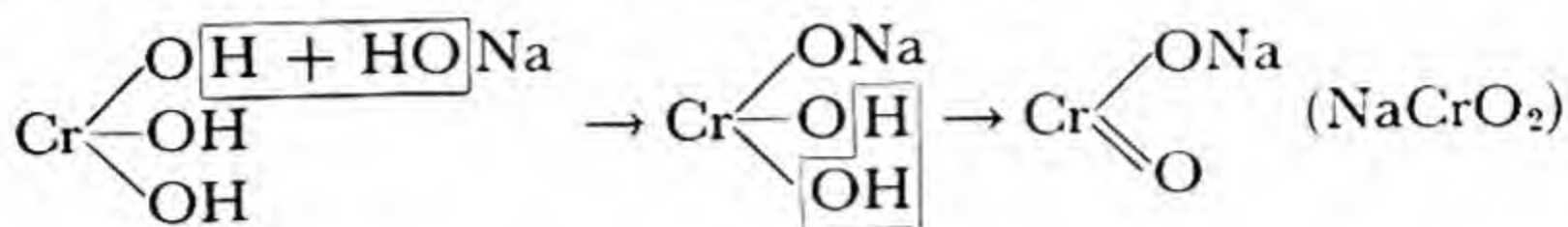


The aldehyde, C_2H_4O , resulting from oxidation of the alcohol is volatile, so only the green solution of chromic chloride is left. Green chromic chloride may also be formed by the action of hydrochloric acid on chromic hydroxide.

The insoluble anhydrous *chromic chloride*, $CrCl_3$, is prepared by the action of chlorine on chromium.

Chromic Hydroxide, $Cr(OH)_3$. This hydroxide is formed as a bluish-green amorphous precipitate when ammonium hydroxide is added to a solution of a chromic salt. The stronger bases could

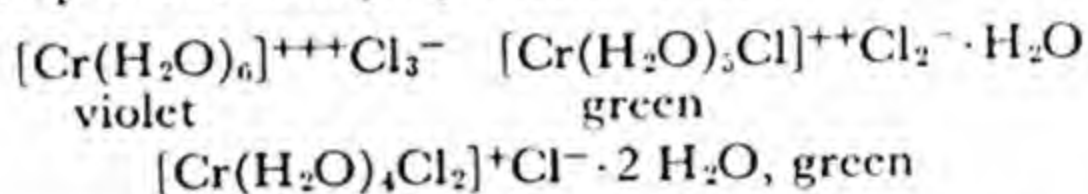
be used, but the hydroxide dissolves in an excess of sodium hydroxide. It is probable that the reaction proceeds as follows:



Chromic hydroxide also dissolves in acids, because it is amphoteric.

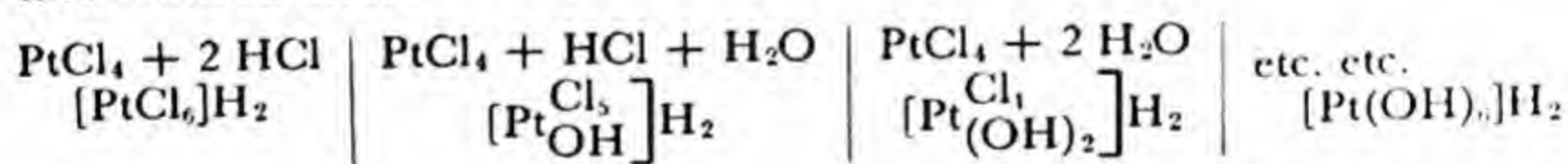
Green and Violet Chromic Salt Solutions. Chromic salts show isomerism, that is, there may be two or more substances of the same composition but different structure and therefore different properties. Chromic chloride $\text{CrCl}_3 \cdot 6 \text{H}_2\text{O}$, yields green solutions usually but may yield a violet solution.

From the violet solution Ag^+ ions precipitate all the chlorine as AgCl . From one green form Ag^+ ions precipitate only two-thirds of the chlorine and from the other green form precipitate only one-third. By Werner's theories (page 486) this difference is due to the existence of complex ions in solution. The chromium atom with its *coordination number* of 6 can hold in a complex ion six groups made up of different proportions of H_2O or Cl .



Only the chlorine outside the complex is ionizable. Werner studied similar series of compounds of platinum, cobalt, and other metals. In many instances the NH_3 molecule played the role of H_2O above.

Platinic chloride shows a coordination series somewhat similar to that of chromium chloride:



Here the coordination number of platinum is six. As stated before, the cupric ion coordinates four NH_3 molecules.

In $\text{K}_4 \cdot \text{Fe}(\text{CN})_6$ the six CN^- ions are coordinated by the central Fe^{++} ion, forming the complex anion, $\text{Fe}(\text{CN})_6^{--}$.

COORDINATION COMPOUNDS

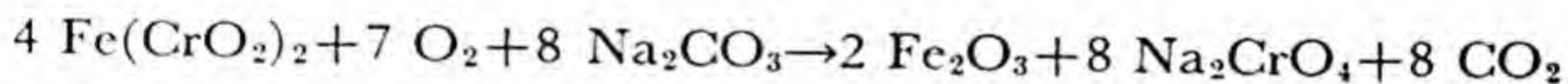
Werner in 1893 stated that each element, or atom, has a definite coordination number — that it can surround itself with a definite number of coordinating groups, usually six although four is common.

The central atom must be large enough for all attached atoms to make contact. In crystallized metals there may be twelve neighbors to each atom. Evidently the ionic radius has a great influence on the coordination number. So does ionic charge but the transition elements' ability to coordinate is far beyond ionic charge influence. The coordination bond is predominately covalent in nature.

The coordination number of lithium and cations of similar size is six. With larger cations (alkali and alkaline earth metals) the number runs up to twelve. The larger the cation the greater the number of anions that can be packed around it.

Water, ammonia, the simpler alcohols, and the halide ions coordinate with nearly all the metals. Water in a crystalline hydrate may (1) coordinate with cations; (2) coordinate with anions; (3) take its place in the crystal lattice; (4) enter into open spaces in indefinite amounts.

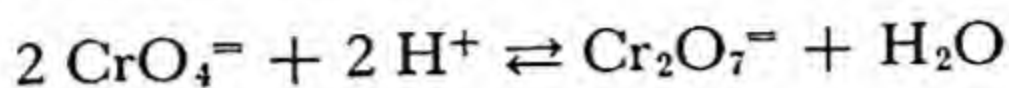
Chromates and Dichromates. The mineral chromite is the starting point in the manufacture of chromates. Fused in the air with potassium hydroxide, or with limestone and sodium carbonate (possibly with addition of a solid oxidizing agent), chromite yields the *soluble* sodium chromate which on addition of acid is converted into the dichromate:



Here the valence of chromium is raised from three to six. Addition of concentrated sulfuric acid to a solid chromate, or dichromate, liberates chromic acid, H_2CrO_4 , or dichromic acid, $\text{H}_2\text{Cr}_2\text{O}_7$, and promptly dehydrates it into the anhydride, CrO_3 . This precipitates in red crystals which readily dissolve in water and rehydrate to the acid.

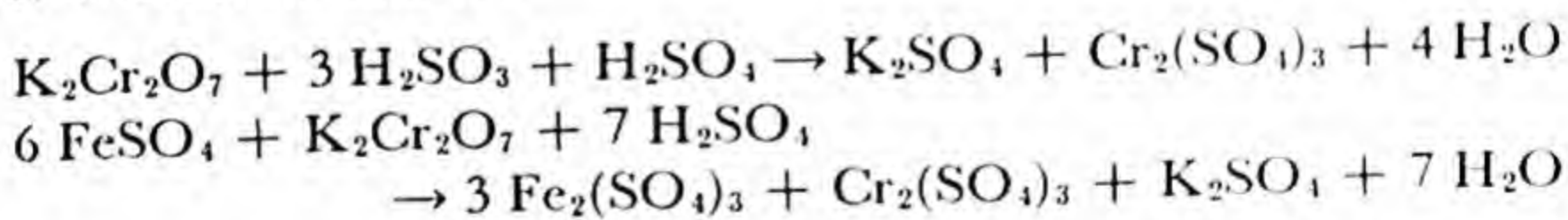
Since potassium dichromate is much more soluble hot than cold, it is easily purified by crystallization. The remarkable change in color from the yellow chromate solutions to the orange-red dichromate solutions on acidifying, with the reverse action on neutralizing with a base, may be explained by supposing that the $\text{CrO}_4^{=}$ ions react with H^+ ions to form $\text{Cr}_2\text{O}_7^{=}$ ions and water.

Both chromate and dichromate solutions may exhibit the following equilibrium condition, shifted one way or another:



Addition of an acid increases the concentration of H^+ ions and drives the reaction to the right. Addition of a base uses up the H^+ ions and drives the reaction to the left. Since both $\text{CrO}_4^{=2}$ and $\text{Cr}_2\text{O}_7^{=2}$ ions are present in a dichromate solution, addition of Pb^{++} ions must result in formation of the more insoluble of the two salts, lead chromate and lead dichromate. **Lead chromate**, PbCrO_4 , is extremely insoluble and is precipitated. It is a yellow pigment used in paints. **Barium chromate**, BaCrO_4 , is a yellow precipitate formed under similar conditions. Sodium dichromate is used to the extent of 22,000 tons yearly in the "chrome tanning" of the lighter skins. It is reduced in the hide to the trioxide (Cr_2O_3), which forms an insoluble compound of some sort with the hide material. "Chrome orange" is basic lead chromate. **Zinc chromate** is greatly used by the Navy as a primary protective coat on metal.

The dichromates are used as commercial oxidizing agents. In oxidizing various substances the chromium usually falls in valence from six to three as illustrated here in the reaction with sulfurous acid. Since the basic oxide, Cr_2O_3 , is liberated in the reduction of a dichromate some extra acid is required to dissolve it as chromic sulfate:



Show the electron transfer as with manganese on page 491.

Chromic acid and a number of chromium salts cause a severe irritation of the skin, so care is required in their handling (as in chrome plating).

Tests. Chromium compounds may be detected by conversion into chromic salts and by addition of sodium peroxide to a little of the very concentrated solution. The soluble yellow sodium

chromate formed is made slightly acid (but not with HCl or H_2SO_4) and treated with a solution of a lead salt. Yellow lead chromate, PbCrO_4 , is precipitated.

Chromium is grouped, in analysis, with ferric iron and aluminum because of the insolubility of its hydroxide. Like that of aluminum its hydroxide dissolves in an excess of base.

When a chromate or dichromate is acidified and shaken with a solution of hydrogen peroxide, blue perchromic acid, HCrO_4 , is formed. It is very unstable in this solution, but if a layer of ether is present the blue compound dissolves in the ether on shaking and lasts for some time. This reaction may be used as a test for chromium or for hydrogen peroxide.

SOME COMPOUNDS OF MANGANESE

(The metal is discussed on pages 510 and 547.)

FORMULA	NAME	SOLUBILITY	REMARKS	
MnO	Manganous oxide	Insoluble	Green	Valence, 2
Mn(OH)_2	Manganous hydroxide	Rather insoluble	Dissolved by NH_4Cl solution	
MnS	Manganous sulfide	Insoluble	Pink-brown	2
$\text{MnSO}_4 \cdot 5 \text{H}_2\text{O}$	Manganous sulfate	Soluble	Pink	2
$\text{MnCl}_2 \cdot 4 \text{H}_2\text{O}$	Manganous chloride	Soluble	Pink	2
MnO_2	Manganese dioxide	Insoluble	Black	4
K_2MnO_4	Potassium manganate	Soluble	Green	6
KMnO_4	Potassium permanganate	Soluble	Purple	7

With chromium, the valence numbers 3 and 6 are important, but with manganese emphasis is placed on valence numbers 2 and 7.

The normal electron arrangement in the manganese atom should be 2, 8, 8, 7 and this is found in the permanganates. In the green manganates it is 2, 8, 9, 6, while in the manganic salts it is 2, 8, 12, 3. Finally in the manganous salts it is 2, 8, 13, 2 with only two valence electrons. The effective atomic radii are for Mn^{++} , 0.91 Å; for Mn^{4+} , 0.52 Å; and for Mn^{7+} , 0.46 Å.

Manganous Compounds. Freshly precipitated manganous hydroxide, Mn(OH)_2 , is of about the same order of solubility as

magnesium hydroxide. Consequently ammonium salts dissolve it just as they dissolve the latter hydroxide. It is all a matter of decrease in OH^- ion concentration, due to the formation of weakly ionized ammonium hydroxide and suppression of its ionization.

Exercise

1. Review the chemistry of magnesium hydroxide and then write the equations for the dissolving of manganous hydroxide in ammonium salt solutions.

Manganese sulfide is the most soluble sulfide of the heavy metals. It is not precipitated by hydrogen sulfide unless a base or a considerable amount of sodium acetate is added. In the usual system of qualitative analysis, this pink sulfide is precipitated by ammonium sulfide. It oxidizes so readily in the air to the soluble manganous sulfate, MnSO_4 , that analysts are accustomed to wash it with hydrogen sulfide water.

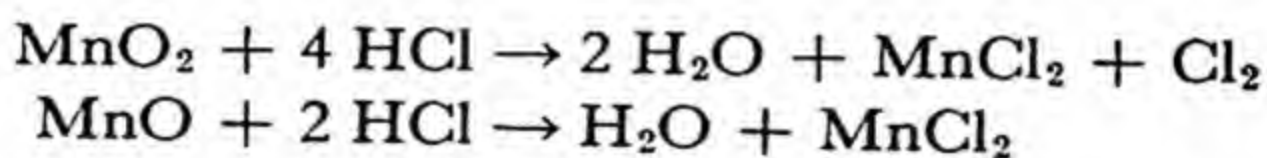
Manganese Dioxide, MnO_2 . Manganese tetrahydroxide, $\text{Mn}(\text{OH})_4$, a very weak acid, readily breaks down into water and manganese dioxide. This oxide is by far the most important compound of manganese. The mineral form is used in dry batteries as a depolarizer. Glass was once decolorized by addition of manganese dioxide. Ferromanganese is made from the dioxide, which is also used to make driers for paints.

TRANSFORMATION BETWEEN MANGANESE COMPOUNDS

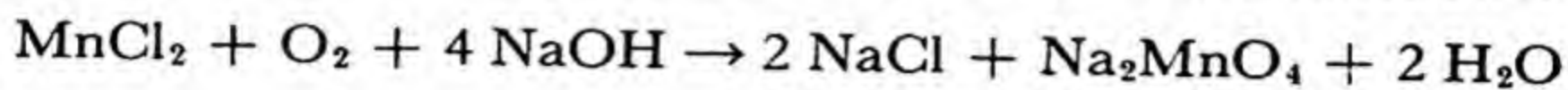
Manganous oxide, MnO , results upon reduction of the other oxides by hydrogen. On the other hand Mn_2O_3 is obtained by heating other oxides of manganese in oxygen. Pure MnO_2 is best prepared by heating $\text{Mn}(\text{NO}_3)_2$. The anhydride of permanganic acid, HMnO_4 is Mn_2O_7 , an explosive oil resulting by contact of concentrated sulfuric acid with the HMnO_4 (released from KMnO_4).

Nearly all the stable oxides tend to give off oxygen and form manganous salts when treated with an acid. If the acid is oxidizable, as hydrochloric, chlorine is released. Thus such salts as

manganous chloride, MnCl_2 , and manganous sulfate, MnSO_4 , are formed:

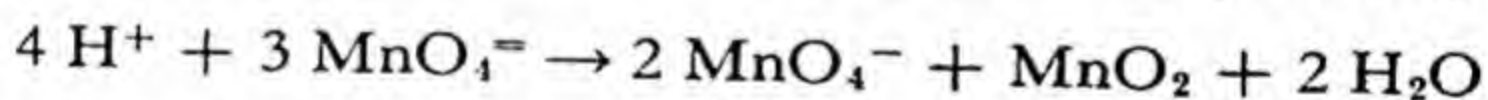


If manganous salts or any oxide are oxidized in the presence of a base, manganese assumes the valence of 6 (as in MnO_3) and green manganates are produced. This is illustrated as follows:

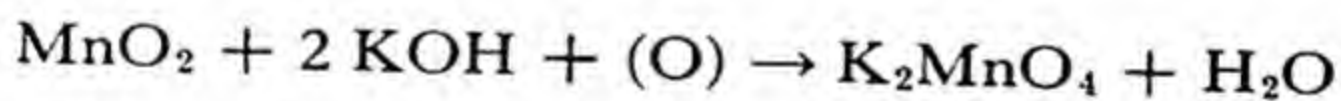


This is equivalent to stating that any oxides of manganese heated in the air with a strong base tend to take up oxygen and yield derivatives of the two highest oxides.

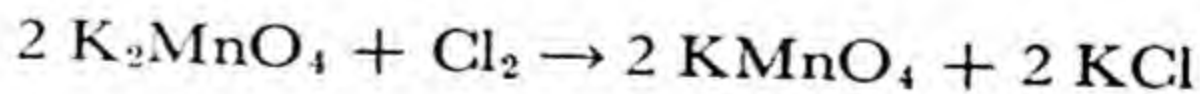
In weakly acid solution (carbonic or acetic) the green manganate ion changes to the purple permanganate ion while MnO_2 is precipitated. In fact this is one way to make the permanganates:



Potassium Permanganate. In the manufacture of *potassium permanganate*, black manganese dioxide is fused with potassium hydroxide in the air:



The fused mass is dissolved in water, forming a green manganate solution, which is then oxidized by chlorine, changing rapidly to a purple color:



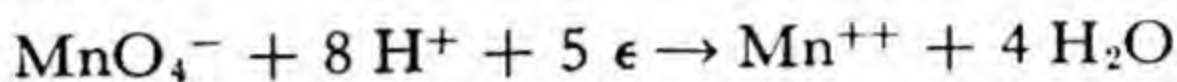
Anodic oxidation of an alkaline solution of the manganate is also a process used commercially.

Permanganates as Oxidizing Agents. Potassium permanganate is very commonly used as a strong oxidizing agent. The reduction of the permanganate amounts in effect to dropping from the oxide, Mn_2O_7 , to one of the lower oxides, MnO_2 , or MnO . The extent of the reduction, and the answer to the question which oxide will be formed, is determined by whether the reduction takes place in basic or acid solution. *In basic or neutral*

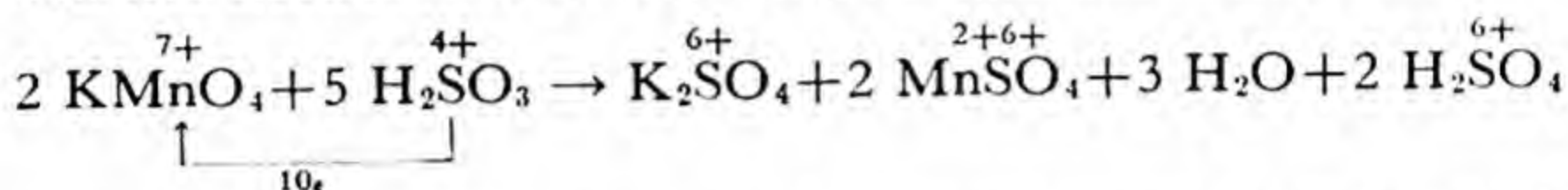
solution manganese dioxide is formed: and in acid solution, the lowest oxide, MnO , which acts most strongly basic. Of course manganous oxide, MnO , would react at once with any acid present to form manganous salts.

The oxidation of hydrogen chloride by potassium permanganate is represented on page 173. It is to be noted, finally, that in acid solution the valence drop is $Mn^{7+} \rightarrow Mn^{2+}$ while in basic solution the change is $Mn^{7+} \rightarrow Mn^{4+}$.

In acid solution:

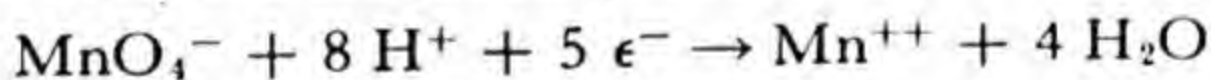


The five electrons are secured from the substance being oxidized:



Solutions of permanganate are so often titrated against reduced iron salt solutions that it is convenient to give the concentration as, for example, "1 ml. $KMnO_4$ solution oxidizes 0.00158 g. of iron from the ferrous to the ferric condition in acid solution."

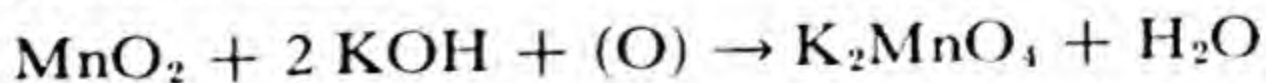
A normal solution of $KMnO_4$ when used as an oxidizing agent is only 0.2 M, if the reduction product is Mn^{++} .



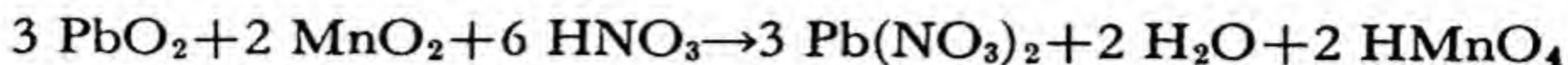
The above equation shows that one mole of permanganate ion accepts five equivalents of negative electricity, therefore a molar solution would have five times normal oxidizing power. In neutral solution with Mn^{4+} as the reduction product the oxidizing power demanded would be different, one mole of permanganate ion accepting only three equivalents of negative electricity.

The same considerations are involved in determining the quantitative concentrations of normal solutions of any oxidizing or reducing agent.

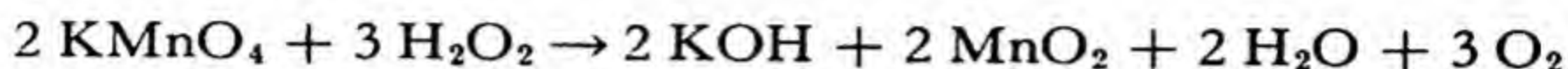
Tests. It is easy to recognize manganese compounds by melting them with potassium hydroxide or sodium carbonate and a little potassium nitrate or chlorate. The green color of the manganate formed is characteristic:



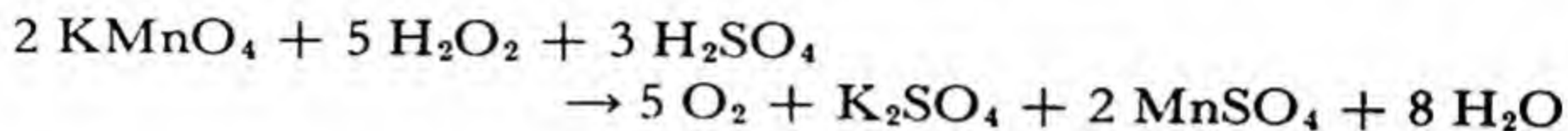
A few drops of a solution of a manganese salt may be boiled with nitric acid in a small beaker and some lead peroxide added. On settling, pink permanganic acid may be seen. Chlorides interfere. Both tests are remarkably delicate:



When hydrogen peroxide is mixed with solutions of potassium permanganate oxygen gas is freely released while a brown precipitate of manganese dioxide forms:



In the presence of dilute sulfuric acid no oxide of manganese is precipitated. Soluble manganese sulfate forms:



Vanadium, Molybdenum, Tungsten,
Uranium, and Platinum

VANADIUM COMPOUNDS

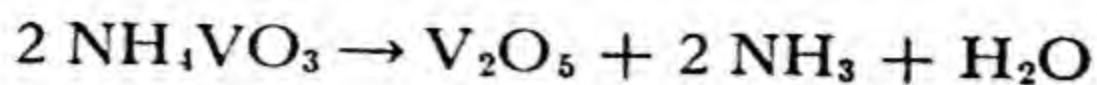
(The metal is discussed on pages 510 and 548.)

This element forms several series of compounds in which the vanadium shows different valence numbers. Vanadium pentoxide, V_2O_5 , is a valuable catalyst (page 280) when properly promoted. Strictly speaking vanadium belongs in Group V.

Fusion of V_2O_5 with alkalis yields such orthovanadates as Na_3VO_4 and K_3VO_4 . V_2O_3 is basic and V_2O_5 acidic.

Reminiscent of the phosphates are sodium metavanadate, NaVO_3 , orthovanadate, Na_3VO_4 , and pyrovanadate, $\text{Na}_4\text{V}_2\text{O}_7$. The Na, K, NH_4 , Ba, and Pb salts of the meta acid are only slightly soluble.

Ammonium metavanadate is precipitated by an excess of ammonium chloride added to a solution of potassium metavanadate. Upon roasting,



Vanadium also shows valence numbers of two and three in compounds and forms a cation, VO^{++} , called vanadyl similar to uranyl ion, UO_2^{++} . It forms salts with most acid anions.

The metavanadates of iron and other metals are used as catalysts in the manufacture of sulfuric acid.

MOLYBDENUM COMPOUNDS

(The metal is discussed on pages 548 and 567.)

On roasting molybdenite, MoS_2 , the *trioxide*, MoO_3 , is formed. This is a yellow-white powder which dissolves readily in sodium hydroxide with the formation of *sodium molybdate*, Na_2MoO_4 . If ammonium molybdate solution is poured into dilute nitric acid, *molybdic acid* is formed. This reagent is used to precipitate orthophosphates as the yellow precipitate $(\text{NH}_4)_3\text{PO}_4 \cdot 12 \text{MoO}_3 \cdot x\text{H}_2\text{O}$. This is the usual procedure in all analytical determinations of phosphorus. The composition of this yellow precipitate is so variable that more accurate results are obtained by dissolving it in ammonium hydroxide and reprecipitating as MgNH_4PO_4 , which is then dried and ignited to be weighed as $\text{Mg}_2\text{P}_2\text{O}_7$.

Ignition of ammonium molybdate yields the trioxide.

TUNGSTEN COMPOUNDS

(The metal is discussed on pages 511 and 548.)

There are four chlorides, WCl_2 , WCl_4 , WCl_5 , and WCl_6 . The hexachloride is formed by passing chlorine over tungsten at 300° . The others are secured by reduction of the hexachloride. The most important oxides are WO_2 and WO_3 . Sodium tungstate, Na_2WO_4 is the best-known salt. It is used to dye and to fireproof fabrics and in making X-ray screens. Many complex tungstates are known. Tungsten carbides were discussed on page 133.

Phosphotungstic acid, useful in the analytic precipitation of proteins and alkaloids, is $\text{H}_3\text{PO}_4 \cdot 12 \text{WO}_3$.

URANIUM COMPOUNDS

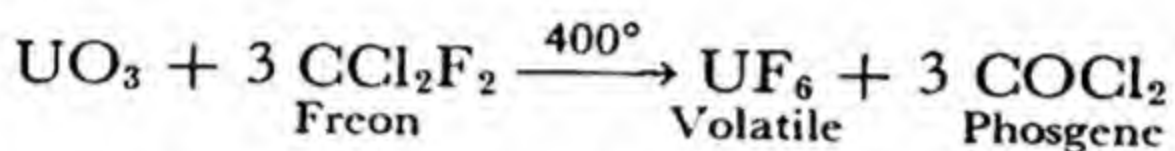
(The metal is discussed on pages 320 and 549.)

In pitchblende, one of the principal uranium ores, the element occurs as U_3O_8 . Hydrates of amphoteric UO_3 are soluble in acids

forming compounds of UO_2^{++} , the uranyl ion. Most of its salts are soluble. Among them are uranyl nitrate, $\text{UO}_2(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$, and uranyl acetate, $\text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2 \text{H}_2\text{O}$. As an acid-forming element it forms such salts as Na_2UO_4 and $\text{Na}_2\text{U}_2\text{O}_7$, the uranates, etc.

Various uranium compounds are used to color glasses and glazes yellow, orange, green, red, and black.

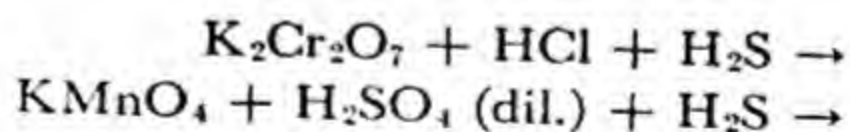
Uranium tetrafluoride, UF_4 , and hexafluoride, UF_6 , were important in the early efforts to isolate U^{235} for atomic bomb purposes.



The gas, UF_6 , is five times as heavy as air and has extraordinary electrical insulation capacity.

Exercises

2. What are the differences between chromic salts and chromates?
3. What is the usual test for a chromium compound?
4. How can we change a manganate to a permanganate?
5. How many liters of H_2S are necessary to decolorize a solution containing 21 g. of potassium permanganate and sufficient sulfuric acid?
6. What weight of SO_2 will be oxidized by 72 g. of KMnO_4 in alkaline solution? In acid solution?
7. Balance



8. How much iodine will be liberated when 25 g. of $\text{K}_2\text{Cr}_2\text{O}_7$ are treated with excess potassium iodide and H_2SO_4 ?

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Chapter 44 COMPOUNDS OF IRON, COBALT AND NICKEL. THE PLATINUM GROUP

SOME COMPOUNDS OF IRON

(The metal is discussed on pages 502 and 549)

FORMULA	NAME	SOLUBILITY	REMARKS
$\text{FeCl}_2 \cdot 4 \text{H}_2\text{O}$	Ferrous chloride	Soluble	Green
$\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$	Ferrous sulfate	Soluble	Cheapest iron salt
$\text{FeCl}_3 \cdot 6 \text{H}_2\text{O}$	Ferric chloride	Soluble	Yellow. Readily hydrolyzed
$\text{Fe}(\text{OH})_3$	Ferric hydroxide	Insoluble	Red-brown
Fe_2O_3	Ferric oxide	Insoluble	Red-brown
Fe_3O_4	Magnetic oxide	Insoluble	Black
$\text{Fe}_2(\text{SO}_4)_3$	Ferric sulfate	Soluble	White. Used in sewage purification
$(\text{NH}_4)_2\text{SO}_4 \cdot \text{FeSO}_4 \cdot 6 \text{H}_2\text{O}$	Ferrous ammonium sulfate	Soluble	Is not an alum. Stable in solid form
$\text{K}_4\text{Fe}(\text{CN})_6$	Potassium ferrocyanide	Soluble	Reagent for Fe^{+++} ions
$\text{K}_3\text{Fe}(\text{CN})_6$	Potassium ferricyanide	Soluble	Reagent for Fe^{++} ions
$\text{Fe}(\text{CO})_5$	Iron carbonyl	Soluble in gasoline	Antiknock qualities

FERROUS COMPOUNDS

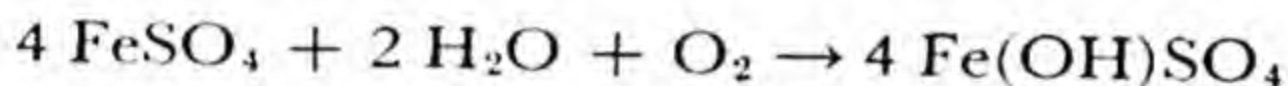
Ferrous oxide, FeO , ignites spontaneously in air. It is prepared by igniting ferrous oxalate in an inert atmosphere.

Ferrous Chloride, FeCl_2 , is prepared by dissolving iron in hydrochloric acid. From this solution it crystallizes as $\text{FeCl}_2 \cdot 4 \text{H}_2\text{O}$,

blue in absence of air, but green in presence of air. Ferrous chloride is easily oxidized:



Ferrous Sulfate, FeSO_4 . Scale (oxide) on iron is removed by immersion in dilute sulfuric acid; ferrous sulfate is formed as a by-product. The crystallized salt, $\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$, is used in water purification because, when added to water with lime, the hydroxide formed drags down dirt and bacteria in settling. Solutions of ferrous sulfate often contain a yellowish precipitate which is basic ferric sulfate, $\text{Fe}(\text{OH})\text{SO}_4$:



A strip of iron and a little free acid prevent this oxidation.

A small amount of ferrous sulfate is used in making iron tannate inks. These contain a dye for immediate color and tannin, which with ferrous sulfate forms ferrous tannate, easily oxidized to black ferric tannate. However, a trace of sulfuric acid prevents this oxidation in the bottle. When applied to the paper, this free acid is neutralized by basic material present and the oxygen of the air converts soluble ferrous tannate into black and insoluble ferric tannate. Ink stains are best removed by treatment with permanganate solution to remove the dye, followed by oxalic acid (10 per cent) to discharge the permanganate and dissolve the iron tannate. Last, washing with dilute ammonium hydroxide removes the acid.

Exercises

1. Write the oxidation equations for the action of dilute nitric acid on ferrous sulfate in the presence of sulfuric acid.
2. Write the equations representing the oxidation of ferrous chloride by potassium permanganate in a dilute hydrochloric acid solution.

FERRIC COMPOUNDS

Red *ferric oxide* Fe_2O_3 , is made by roasting iron pyrites, FeS_2 , or by heating $\text{Fe}(\text{OH})_3$. Black Fe_3O_4 forms on hot steel as it is shaped in the mill.

Ferric Hydroxide. This gelatinous precipitate is thrown down when any soluble base is added to a solution of a ferric salt. It dissolves in acids but not in alkalies (unlike the hydroxides of chromium and aluminum).

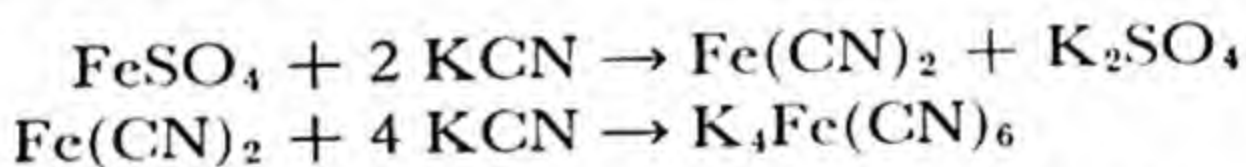
Ferric Chloride, $\text{FeCl}_3 \cdot 6 \text{H}_2\text{O}$. The preparation of ferric chloride consists in passing chlorine into a solution of ferrous chloride. The yellow, deliquescent, and very soluble solid secured by partial evaporation of the solution is hydrolyzed to such an extent that on heating it to dryness nothing but the oxide, Fe_2O_3 , remains. The *anhydrous form* must be prepared by passing chlorine over hot iron.

Unlike most salts, anhydrous ferric chloride is soluble in some organic solvents, apparently because of a low degree of polarity.

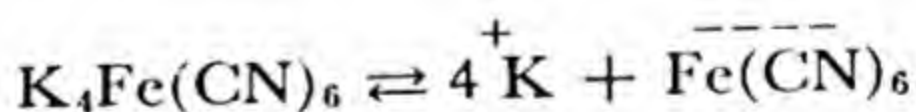
Ferric Sulfate, $\text{Fe}_2(\text{SO}_4)_3$. Ferric sulfate, formed by oxidation of ferrous sulfate, is now used chiefly in purification of water and in the coagulation of sewage.

THE COMPLEX CYANIDES OF IRON

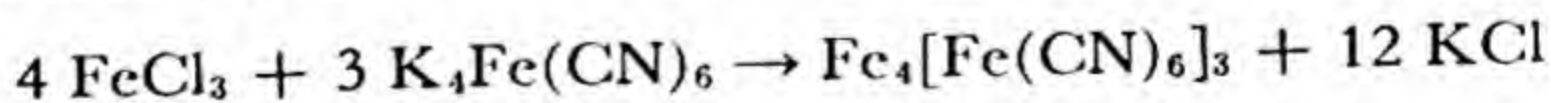
Addition of potassium cyanide to a solution of a ferrous salt produces a precipitate of ferrous cyanide, readily soluble in an excess of the reagent:



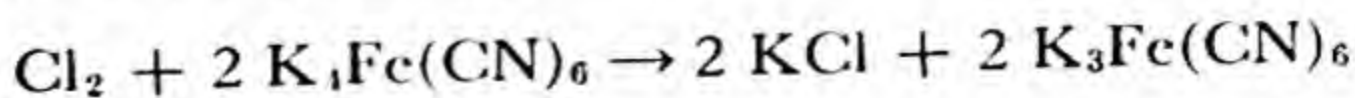
The complex salt, potassium ferrocyanide, $\text{K}_4\text{Fe}(\text{CN})_6$, ionizes as follows:



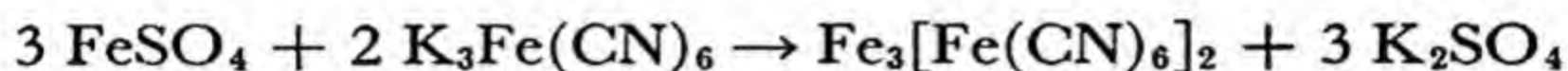
The ferrocyanide ion is very stable, yielding no simple iron ions. With ferric salts there is formed a precipitate called Prussian blue which is really ferric ferrocyanide:



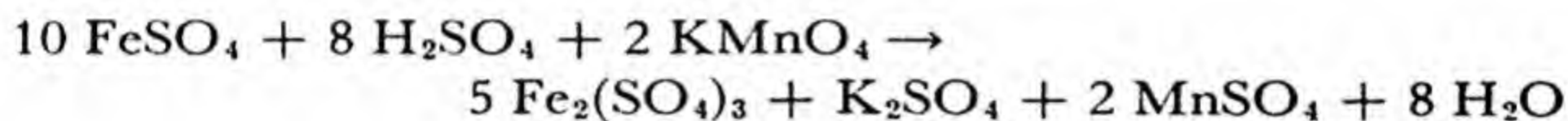
When chlorine is passed into a solution of the yellow potassium ferrocyanide the reddish potassium ferricyanide is formed:



This salt reacts with ferrous salts to form insoluble Turnbull's blue, which is ferrous ferricyanide:



Iron is conveniently determined quantitatively by titrating a purple potassium permanganate solution of known concentration (standard solution) against a known volume of the ferrous salt solution. As a preliminary the iron salt must be reduced completely by hydrogen or any other agent which can be removed completely after the reduction is achieved:



The purple solution is cautiously added from a burette until a final drop gives the solution a persistent color. Then from the volumes used and the relative weights revealed by the equation above it is possible to calculate the amount of iron reacting. In this reaction iron changes from Fe^{++} to Fe^{+++} by the loss of one electron while manganese changes from Mn^{7+} to Mn^{++} by the gain of five electrons.

Tests. Ferrous salts are recognized by reaction with potassium ferricyanide to form Turnbull's blue. Ferric salts react with any alkali thiocyanate to form soluble, red ferric thiocyanate. They also react with potassium ferrocyanide to form insoluble Prussian blue. Ferric hydroxide is red, insoluble, and differs from the hydroxides of chromium and aluminum in not dissolving in sodium hydroxide.

COBALT COMPOUNDS

(The metal is discussed on pages 515 and 550.)

A full set of cobaltous salts (derived from CoO) is known but of the cobaltic salts only complex cobaltic salts (derived from Co_2O_3) are stable. The writing done with a pale pink cobalt salt solution (CoCl_2 , usually) is invisible, but on drying cautiously over a flame the blue color of the anhydrous salt becomes conspicuous. Cobalt salts are used as driers in paints, varnishes, and linoleum.

The dioxide, CoO_2 (like NiO_2), is formed by vigorous oxidation of Co^{++} . It forms cobaltites. *Potassium cobaltinitrite*, $\text{K}_3\text{Co}(\text{NO}_3)_6$, only slightly soluble, is formed from Co^{++} , K^+ , NO_2^- ions in presence of acetic acid.

NICKEL COMPOUNDS

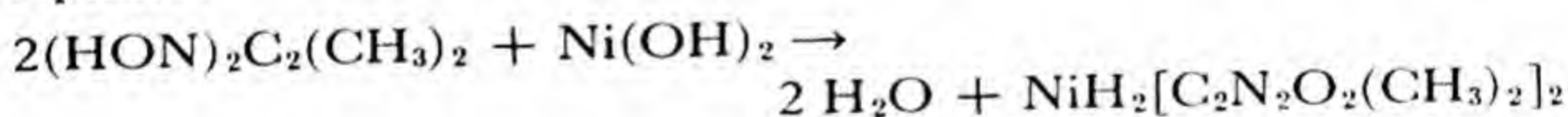
(The metal is discussed on pages 515 and 550.)

Nickel Compounds. There are two series of nickel salts derived from nickelous oxide, NiO , and nickelic oxide, Ni_2O_3 . All ordinary nickel salts are green when hydrated. Nickel sulfide, NiS , is precipitated as a black powder when ammonium sulfide is added to a solution of a nickel salt. Many nickelous salts are known but nickelic salts are unstable. The green $\text{NiCl}_2 \cdot 6 \text{H}_2\text{O}$, and $\text{NiSO}_4 \cdot 7 \text{H}_2\text{O}$ are common salts of this metal.

Nickel and nickel oxide catalysts have extensive use as aids in the preparation of some organic chemicals. The hydrogenation of fats was the first catalytic hydrogenation to attract much attention.

TESTS FOR NICKEL AND COBALT

Nickel salts react with dimethylglyoxime to give a scarlet precipitate:



Cobalt compounds give a blue bead with borax or microcosmic salt, but with the same substances nickel compounds yield a brown bead in the oxidizing flame. Cobalt salts react with nitroso- β -naphthol to yield a brick-red precipitate, and in the presence of ammonia react with phenylthiohydantoic acid to yield a red-brown precipitate.

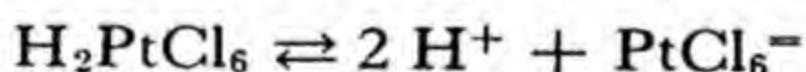
3. What is the formula of an iron oxide which contains 27.6 per cent oxygen and has a molecular weight of 232?
4. How could you convert 15 selected metals into one useful compound each?
5. Give one commercial use of a dichromate; of manganese dioxide.
6. A reagent bottle half filled with ferrous sulfate solution, FeSO_4 , gradually shows a brown precipitate. What is it? Upon adding some dilute sulfuric acid and an iron nail the precipitate slowly disappears. Explain.

PLATINUM COMPOUNDS

(The metal is discussed on pages 550 and 551.)

Platinum forms two series of compounds in which it has valence numbers of 2 and 4. *Platinum chloride*, PtCl_2 , is formed when chlorine is passed over the finely divided metal at 240° – 250° . With hydrochloric acid it forms chloroplatinous acid, H_2PtCl_4 . The potassium salt, K_2PtCl_4 , is used in photography. Black platinous hydroxide, $\text{Pt}(\text{OH})_2$, is formed by addition of a base to a solution of platinous chloride. On gentle heating the hydroxide yields the oxide and at higher temperatures the metal itself. Barium platinocyanide, $\text{BaPt}(\text{CN})_4 \cdot 4 \text{H}_2\text{O}$, fluoresces when bombarded by X-rays and hence is used for X-ray screens.

Platinum dissolves in aqua regia with formation of the soluble *chloroplatinic acid*, H_2PtCl_6 . This is the reagent used in the quantitative determination of potassium, because the potassium salt, K_2PtCl_6 , is insoluble. That the acid ionizes as follows:



is proved by addition of silver nitrate. No silver chloride is precipitated, only silver chloroplatinate, Ag_2PtCl_6 .

Platinic chloride, PtCl_4 , is formed by heating chloroplatinic acid in a current of chlorine at 360° but is itself decomposed above 500° . Similar compounds of *palladium* are known.

Rhodium compounds are derived from RhO , Rh_2O_3 , and RhO_2 .

Iridium has two series of salts, with valence numbers 3 and 4; for example the green $\text{K}_3\text{IrCl}_6 \cdot 3 \text{H}_2\text{O}$ and the red K_2IrCl_6 .

Osmium compounds are of little interest except the poisonous OsO_4 , wrongly called "osmic acid."

Exercises

7. How does an iron ink operate?
8. Evaporate a solution of ferric chloride to dryness. What have you? Why?

References

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- Kettering, C. F. "Chemistry of the Motor Car". *Chem. Eng. News*, 21, 841 (1943).

Chapter 45 PREPARATION OF THE METALS. PART I

Extraction from Ores. When a metal occurs in the free state (gold, copper in the Lake Michigan area, and a few other inactive metals) it can readily be separated from the rock or other materials associated with it. However, most metals must be won from such ores or salts as oxides, sulfides, carbonates, sulfates, chlorides, and fluorides. Scrap metal is usually recovered by melting. The secondary or scrap metals (Cu, Al, Zn, Pb, Sn, Ni, Sb) recovered annually in this country are worth \$250,000,000.

The eight processes (broadly treated) used in metallurgy are:

1. Reduction of oxides with carbon
2. Reduction with aluminum (thermit process)
3. Reduction with hydrogen
4. Roasting sulfides
5. Roasting sulfides with carbon
6. Electrolysis of fused salts
7. Amalgamation with mercury
8. Cyanide extraction

Copper is prepared by first roasting the sulfide ore but the crude product finally must be purified for electrical uses by electrolysis of a water solution of a copper salt.

HEATS OF FORMATION OF METALLIC OXIDES

In Calories per Formula Weight in Grams
(The negative sign means that heat is absorbed)

Au_2O_3	-11,000	ZnO	+ 85,000
Ag_2O	+ 6,953	MgO	+146,100
CuO	+38,500	Fe_2O_3	+198,500
PbO	+52,470	SiO_2	+201,400
NiO	+58,400	Al_2O_3	+399,000

The compounds with the highest heats of formation are the most stable, and require the greatest amount of energy for recovery of the metal.

Reduction with Carbon: Fe, Zn, Cd, Sn, Cr, Mn, V

IRON

Iron was used to a very limited extent in Egypt as early as 4000 B.C. but the Hindoos about 2000 B.C. developed the industry of smelting iron from its ores. This early iron, because of low temperatures, was spongy but not fluid, and had to be hammered into shape.

Occurrence. Free iron in nature is rare. A little occurs in meteorites. Hematite, Fe_2O_3 , furnishes the world with, by far, the greater part of its iron. Limonite, $2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, is a yellowish ore, while magnetite, Fe_3O_4 , is a black oxide, supplying only 5 per cent of the world's iron. In addition to the workable ore beds there are iron oxides in clays which add to the beauty of coloring that is so conspicuous in Yellowstone Park and elsewhere. Bricks owe their colors to such oxides.

Since the richest iron ore beds around Lake Superior will be exhausted in a generation it will be necessary to develop the metallurgy of the adjoining low-grade ores. "Taconite," a complex ore containing magnetite, hematite and the carbonate has not yet been used, yet there is enough in Minnesota to supply us for centuries — if the metallurgical problems are solved.

The United States has the richest iron ore deposits now being mined, but Morocco has extensive unworked beds and Brazil is said to have the largest and richest deposit of all — now being developed with United States aid. Germany and Russia also have large ore beds. An enormous deposit has been discovered in Labrador.

Metallurgy. Carbonates of iron are converted into oxides on heating, and oxides are reduced by heating in contact with coke and limestone. Great Britain utilizes carbonate ores and some day we shall mine the rich magnetite ores (Fe_3O_4) of Alaska.

In ancient days the charcoal for reduction of the iron oxide ore was fed a feeble blast of air from a foot bellows. In the 14th cen-

tury a water wheel increased the blast but it was not until 1860 that the steam engine operated blowers and large-scale production of crude iron became a reality. Coke began to supplant charcoal about 1720.

There is no technical reason why we should not reduce iron ores with natural gas.



Fig. 135. Ancient iron furnace.

The Blast Furnace. Iron was made many centuries ago, but its manufacture on a vast scale did not become possible until 1619 when coal or coke was first used as the reducing agent.

Modern blast furnaces are of giant proportions (Fig. 136). Most of them are 90 ft. high and some are higher. The greatest diameter is usually about 20–25 ft. They are built of heavy steel plates lined with fire brick. The lower part where the heat is more intense is usually bound with water-cooled bronze blocks set in the brick wall. At the top of the “stack,” as the furnace is called, are double bell-shaped doors which admit the ore, coke, and limestone without undue loss of gases. Below this point the stack steadily widens to allow for expansion of the charge. But at a certain point fusion of part of the material causes such a great decrease in volume that the stack tapers in accordingly. Otherwise the heavy charge would fall and burst the furnace. The narrowing part is called the “bosh.” Just below this is the “crucible” in which molten iron and slag accumulate. The tap hole for iron is at the bottom, but the “cinder notch” for the slag is a little higher. Just above the crucible are several openings called “tuyères,” through which a great blast of heated air is blown to burn the coke. From 40,000 to 50,000 cubic feet of air per minute

at 15 to 20 lbs. pressure are required. The pasty particles of free iron do not melt until they have dissolved enough impurities, such as sulfur, silicon, and carbon, to lower the melting point sufficiently. The melted iron runs in the crucible, while the lighter

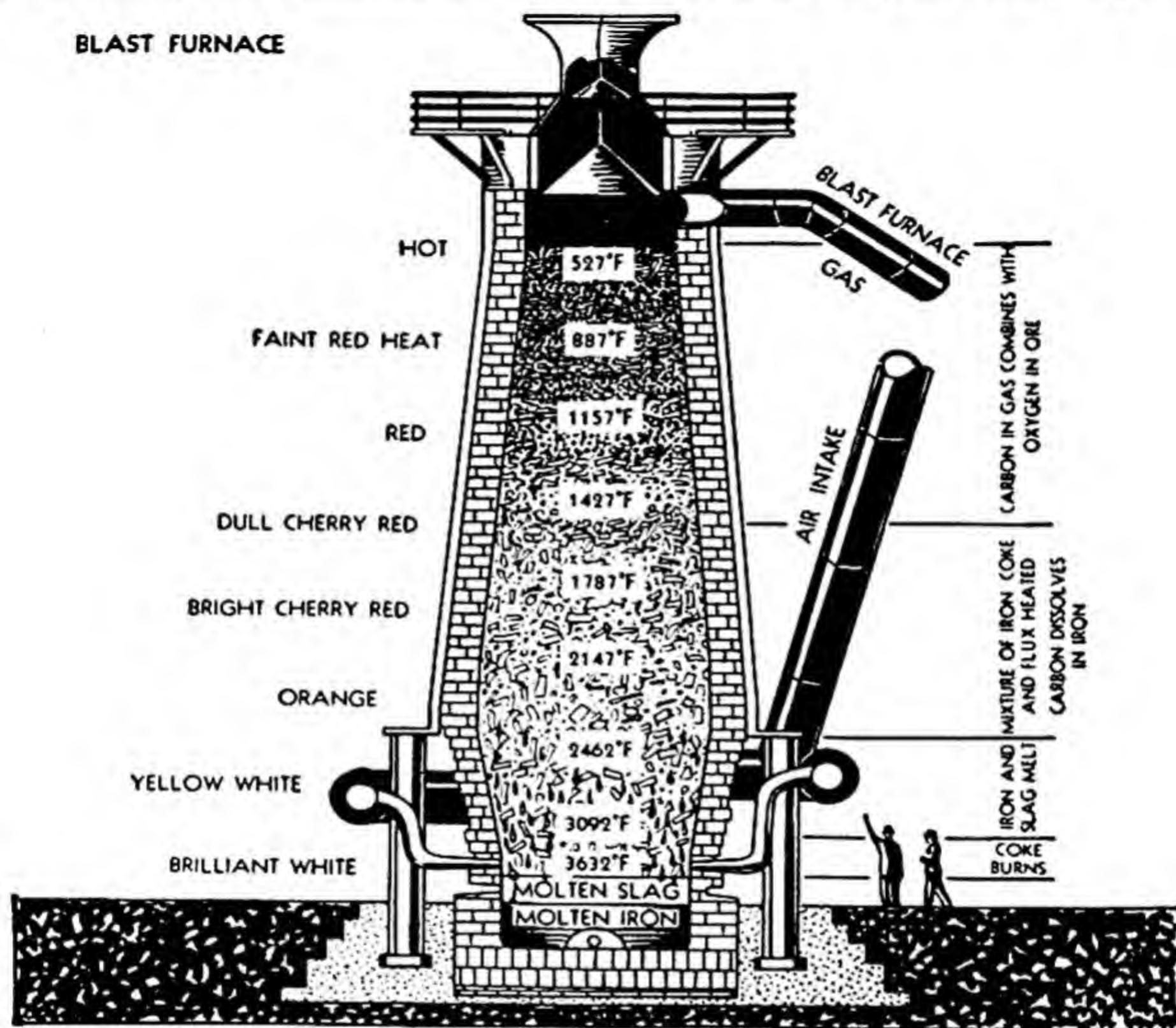


Fig. 136. The blast furnace. (Courtesy General Motors Company.)

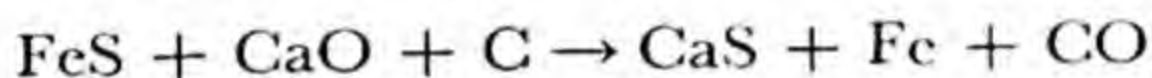
fluid slag floats on top. At the top of the bosh the temperature is 1350° , and at the top of the crucible about 1700° . The equations representing the essential reactions in the blast furnace follow:

1. $\text{Coke} + \text{hot-air blast} \rightarrow \text{CO}_2$
2. $\text{Hot C} + \text{CO}_2 \rightarrow 2 \text{CO}$
3. $\text{Fe}_2\text{O}_3 + 3 \text{CO} \rightarrow 2 \text{Fe} + 3 \text{CO}_2$
4. $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$
5. $\text{CaO} + \text{SiO}_2 + \text{Al}_2\text{O}_3 \rightarrow \text{Calcium silicate and calcium aluminate, in the slag}$

Possibly FeO and Fe_3O_4 also enter into this series of reactions. The iron is tapped off every 6 hours, but the slag is removed more frequently. The iron is run into molds from which the solid "pigs" are removed or it may be carried in great ladles to the steel mill without solidifying. **Slag** is carried away in ladles to the dump or is granulated by pouring into water. In this form it is easy to handle as railroad ballast or as a raw material for Portland cement. Since it is a complex calcium aluminum silicate, slag needs only to be burned with more lime and ground to produce a very fair grade of hydraulic cement.

The slag, formed from oxides of Fe, Si, Al, Ca, Mg, etc. must be fluid but not too fluid or it drops so fast that it fails to remove all the sulfur. Manganese sulfide, insoluble in pig iron, dissolves in the slag.

Coke always carries from 0.5 to 2.0 per cent of sulfur which unfortunately is picked up by the hot iron. But as drops of melted iron fall through melted slag the sulfur happily is largely removed from the iron. The essential reaction follows:



The gases from the top of the stack are burned or fed to gas engines for power. In composition they approximate producer gas and have a fuel value of 100 B. T. U. per cubic foot. There is a gain in using this gas at once because it leaves the stack at about 400° . About one-third the stack gas is burned directly in a series of "stoves," steel towers filled with an open checkerwork of fire brick, which becomes highly heated. The air blast is then preheated by passage through these hot stoves. It is necessary to preheat the air blast in order to secure the proper temperature in the blast furnace.

CHARGE	PRODUCTS
1 ton ore	1120 lbs. pig iron
1000 lbs. coke	800 lbs. slag
500 lbs. limestone	3 tons gases (N_2 , CO_2 , CO , H_2O)
3 tons air	

Cast (Pig) Iron. The product of the blast furnace is termed pig iron. It is only about 92–94 per cent iron, the usual impurities

being about 3 per cent carbon along with some silicon, manganese, sulfur, and phosphorus. Much of this iron is cast into pigs, for convenience in handling, and then shipped to the various markets. It is remelted at the foundries (by coke in a cupola) and cast into such shapes as are needed for radiators, stoves, wheels, and a thousand useful articles. Pig iron is cast iron, but there are two types, depending on the rate of cooling. If poured into a metallic mold so that the liquid is chilled suddenly, the carbon does not have time to separate as graphite, but remains uniformly distributed as cementite, Fe_3C . The product is white, very hard, and very brittle. If cooled more slowly in sand molds, gray cast iron results. In this, part of the carbon has had time to separate as graphite. This gray cast iron is not nearly so hard as the white variety and can be given some ductility if annealed a few days. Cast iron alloyed with a little Ni, Cr, or Cu, resists corrosion and high temperatures better.

Such metal melts at about 1150° , while pure iron melts at about 1535° . Cast iron is hard, but low in tensile strength. It cannot be welded or forged, but it expands enough on cooling to fill a mold completely.

Malleable iron is made by holding cast iron at a bright red heat for two or three days. It is stronger and more shock-resistant.

Soft cast iron owes its character to the 3 to 3.5 per cent of carbon, present largely as graphite. The manufacturer controls the condition of the carbon mainly by the addition of silicon and by the rate of cooling. At least eighteen elements have been used in alloy cast irons.

Wrought Iron. To make a tough iron suitable for anchors, horseshoes, etc., it has long been the practice to purify melted pig iron on a bed of iron oxide in the *puddling furnace*. This is merely a small reverberatory furnace so built that heat is reflected and radiated down on the charge from the low roof of the furnace (Fig. 137). The pig iron melts, but as the impurities are burned out by the oxygen of the scale or ore, its melting point rises and the metal becomes plastic rather than fluid. Limestone may be added as a flux. The metal is worked by the "puddler," using a

long "rabble," and is finally removed in balls weighing about 100 pounds. Under the hammer or in the rolls the fluid slag is squeezed out, leaving nearly pure iron as fibers separated by thin films of slag. The slag is not dissolved in the iron. The product is extremely tough and strong, but not as hard as cast iron.

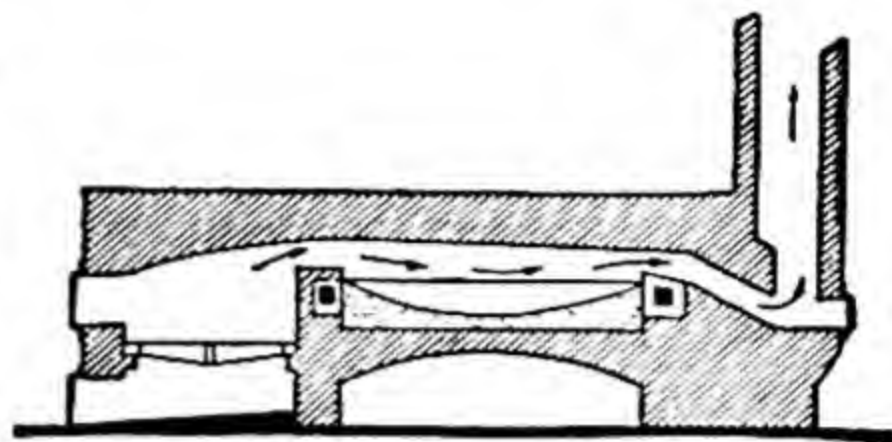


Fig. 137. Puddling furnace.

In recent years wrought iron has been largely replaced by low-carbon steel (0.2 per cent carbon or less), which is just as tough and is made more rapidly.

In 1929 commercial efforts were made to produce wrought iron on a large scale by pouring melted pig iron, after Bessemerizing, into melted slag (Aston process). The gases liberated caused the dispersion of the metal into fine drops. The iron-slag mixture was rolled in the usual way to reduce the slag content and give the mass tough fibrous structure. The quality of the product compares very favorably with that of hand-wrought iron.

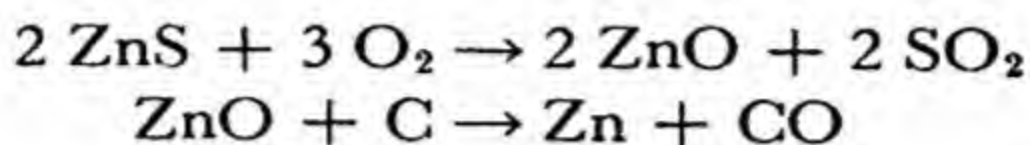
(Steel will be discussed in the chapter on Alloys.)

Sponge Iron. The U. S. Bureau of Mines has worked out the details of operation of furnaces using natural gas or gases from coal to reduce iron ores. The product is soft sponge iron, not molten metal. One advantage is that small furnaces may profitably be located near small ore deposits and can operate on lower-grade ores. Also the high-purity soft iron (nearly free from carbon) is already in demand for magnet cores and armatures. It is interesting to note that the primitive iron furnaces of earlier centuries also produced soft sponge iron which was hammered into tools and weapons.

ZINC

Occurrence. The world usually produces 1,200,000 tons of smelter zinc in a year and of this the United States accounts for 600,000 tons. Sphalerite or zinc blende, ZnS , and smithsonite, ZnCO_3 , are the chief ores in the western United States.

Metallurgy. Many zinc ores need to be concentrated before smelting can be profitable, so the oil-flotation process is used as with copper sulfide ores. Oxides or carbonates need only to be heated with coal to be reduced to the metal. Sulfides must be heated with excess air to secure the oxide of zinc, which is then further heated with carbon to secure its reduction. In some smelters a sulfuric acid plant is attached to utilize the sulfur dioxide:



The zinc oxide and coal are heated in fire-clay retorts. The zinc is volatilized and then condensed in receiving vessels. Carbon monoxide burns at the mouth of each receiver. Since zinc boils at 925° and the temperature at which the reduction occurs is 1200° , it is evident that the vapor of the metal must be formed. When the vapors are led into cold receivers at any temperature below 415° (melting point of zinc), only zinc dust is obtained, but after the hot vapors heat the receivers above 415° only the liquid form is condensed. This is cast into slabs called spelter. It may be purified by electrolysis. (See Copper.)

CADMIUM

Occurrence and Preparation. Cadmium occurs in small quantities in zinc ores. Being more volatile than zinc it is found in the first distillate, from which it can be separated by fractional redistillation (in an atmosphere of hydrogen to prevent oxidation) and by electrolytic purification. Western zinc spelter carries about 0.4 per cent cadmium. This cadmium does some harm, but the cost of its removal is discouraging.

TIN

Occurrence. Tin ores are so easily smelted that the metal was known to the ancients. At present most of it comes from the East Indies, the Malay States, Siam, and Bolivia, although China and Nigeria are large producers. The chief ore is the crude dioxide, SnO_2 , called cassiterite or tin stone.

Metallurgy. All tin ores are concentrated by washing away the "gangue," and they are then roasted in long rotary kilns like Portland cement kilns. By this process the sulfur is oxidized to the dioxide. Arsenic is oxidized to the trioxide, which is collected in a cooling chamber — later to be sold as a valuable by-product. After this preliminary roasting the tin oxide is heated with carbon in a furnace, where it is reduced to the metal. In order to separate the tin from the bismuth, zinc, copper, and iron, which are usually present with it, advantage is taken of the surprisingly low melting point of the pure metal, 231.85° . The foreign metals are present as higher-melting tin alloys. The mass is heated hot enough to melt pure tin, but not hot enough to melt the alloys.

In a normal year the world produces 150,000 tons of tin, and the United States uses more than half of this amount — 90,000 tons including recovered scrap.

CHROMIUM

Occurrence. The only important chromium ore for commercial purposes is chromite, $\text{Fe}(\text{CrO}_2)_2$, sometimes written, $\text{FeO} \cdot \text{Cr}_2\text{O}_3$. It is mined in Rhodesia, India, Cuba, Turkey, Portuguese Africa, New Caledonia (near Australia), Russia, and the Philippines. California produced large amounts in a war emergency.

We imported yearly 400,000 tons of chromite, out of the world production of one million tons, until World War II when we were forced to develop a huge chromite ore deposit in Montana; this ore is low-grade but is workable after enrichment. It is possible for us to lead the world in the production of "ferrochrome."

Metallurgy. Until the recent development of chromium plating the free element was not prepared in great quantity, as its alloy with iron is cheaper and more suitable for steel making. Most of this alloy, "ferrochrome," is made by the reduction of chromite with carbon in the electric furnace. A small amount of the carbon-free alloy is made by the thermit process, page 510.

It is possible to treat low-grade ore with hot chlorine to form volatile CrCl_3 which can be reduced by hydrogen to yield almost pure metal.

MANGANESE

Occurrence. The chief manganese ore is pyrolusite, MnO_2 , which is mined in India, Russia, West Africa, Cuba, and Brazil.

In the past we depended upon importations of high-grade ores suitable for the manufacture of ferromanganese. Our own low-grade ores can be concentrated in a war crisis.

Metallurgy. Manganese is rather difficult to prepare because, although the oxides are reduced with carbon in the electric furnace or blast furnace, some carbon unites with the metal. The pure element is prepared by the thermit process. Commercially the metal is of value mainly in the form of an alloy with iron. Such an alloy carrying less than 20 per cent manganese is called *spiegeleisen*, while an alloy carrying from 20 to 90 per cent is called *ferromanganese*. These alloys, about 12 pounds to the ton, are added to steel as scavengers and to give it hardness, strength and ductility.

Low-grade manganese ores may be added to the blast-furnace charge in order to improve the pig iron. In 1948 we produced 1,136,000 tons of ores carrying from 5 to 35 per cent manganese, and some of the ores contained both manganese and iron.

The U. S. Bureau of Mines has recently devised a process of leaching low-grade manganese ores (plentiful in this country) and winning this vital metal by electrolysis under exactly controlled conditions of acidity and concentration. The product is 99.94 per cent pure.

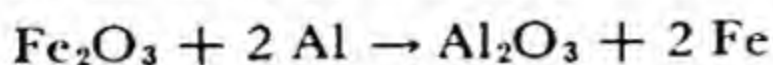
VANADIUM

Peru and the United States have the most important deposits of vanadium ore. In 1943 enormous deposits were found in Idaho. Rhodesia and S. W. Africa also have ore deposits. Reduction of the ores by carbon in a vacuum furnace is common practice. Ferro-vanadium is easier to prepare than vanadium itself and is the material used in the steel industry. Vanadium produces a finer grain in steel, increasing the elastic limit.

Reduction with Aluminum. Thermit Process

"Aluminothermy" is a process developed by Goldschmidt, who discovered that powdered aluminum when ignited reduces many metallic oxides with the

evolution of a great amount of heat. Temperatures of 3000° are obtained so that the metal is molten and may be cast in a mold:



The heat of formation of Al_2O_3 is 392,600 cal., while the heat of decomposition of Fe_2O_3 is 197,000 cal., so 195,600 cal. are freed. If a shaft on a ship at sea were broken, the ends could be welded together by surrounding them with a sand or clay mold and igniting a mixture of iron oxide and aluminum powder (thermit) in a funnel above. The melted iron runs into the mold, melts the broken ends of the shaft, and produces a perfect union. In actual practice the shaft ends are preheated.

Since the heat of formation of magnesium oxide is greater than that of aluminum oxide it is evident that aluminum will not reduce magnesium oxide.

Reduction of the oxide of manganese is typical:



Incendiary bombs may contain thermit mixtures.

COBALT AND NICKEL

Cobalt occurs with nickel and arsenic. Smaltite, CoAs_2 , is also known. South Africa and Canada are the chief producers. The metal is best prepared by the thermit process. Carbon-free nickel is prepared the same way. The leading nickel process is discussed on page 515.

Reduction with Hydrogen

TUNGSTEN

Tungsten is now considered one of the "key metals" of industry, occupying fifth place among the first ten essential metals of modern civilization. The chief ore is ferrous manganese tungstate, $[\text{Fe}, \text{Mn}]\text{WO}_4$, called wolframite. China leads in production, followed by the United States, Australia, Argentina, Burma, Spain, Portugal, and Rhodesia.

Wolframite is fused with sodium carbonate and the sodium tungstate, $\text{Na}_2\text{WO}_4 \cdot 2 \text{H}_2\text{O}$, formed is extracted with hot water. When this salt is treated with acids the free tungstic acid, $\text{H}_2\text{WO}_4 \cdot \text{H}_2\text{O}$, is precipitated, and when this is ignited the oxide, WO_3 , is secured. This oxide may be reduced by carbon or by the aluminothermic process, or by hydrogen in an electrically heated furnace at 1000° , or above.

The metal is obtained as a powder on reduction of the oxide and is worked into strong filaments or rods. By the new Fink process low-grade ores are electrolyzed in fused borate or phosphate baths. It has been found that the only way to secure strong compact tungsten is to work it while very hot (but not melted) in a reducing atmosphere of hydrogen. If desired in sheet form, it is hammered and rolled, but if desired for wire it is drawn finer and finer until it is strong enough to be pulled through diamond dies and reduced to the diameter needed for lamp filaments.

Since *tantalum* becomes brittle by absorbing hydrogen it must be heated in a vacuum to drive out gases and then worked cold.

Exercises

1. What is the function of the slag in the blast furnace?
2. Why aren't all metals obtained by reduction with hot hydrogen?
3. How could the thermit process be used in emergency welding of a broken rod on a locomotive?

Chapter 46 PREPARATION OF THE METALS. PART II

Roasting Sulfides in Air: Cu, Ni, Hg, Ag, Mo

COPPER

The ease of extraction of copper from ores containing the free metal made copper one of the first metals known to man.

The oldest piece of pipe on record is a copper tube from the tomb of an Egyptian king who reigned about 2900 B.C. This tube is 40 inches long and 3.5 inches in diameter, formed by hammering a sheet of the metal around a mandrel.

Occurrence. The world normally produces about 2,400,000 metric tons¹ of copper per year and of this total the United States furnishes about one-third. Africa, Chile, Mexico, Japan, Canada, Russia, and Spain supply the rest. A large deposit of free copper occurs in Michigan near Lake Superior, but the chief ores are chalcocite, Cu_2S , and copper pyrites, CuFeS_2 , found in Montana and Utah. Malachite, $\text{Cu}_2(\text{OH})_2\text{CO}_3$, and the similar azurite occur in Arizona. California, New Mexico, Tennessee, and Alaska also possess great deposits of rich copper ores.

METALLURGY OF COPPER

Sulfide ores, containing iron, clay, etc.

1. Concentration of ore from 3 per cent (or less) to about 8 per cent
 - { Crushing
 - { Wet-settling
 - { Froth-flotation

¹ A metric ton is 1000 kg. or about 10 per cent more than our common short ton.

2. Roasting in air to remove 80 per cent of sulfur as SO_2 . The 20 per cent remaining is needed to form fusible "matte" of sulfides, for step 4.
3. Smelting of roasted ore in reverberatory furnace (reflected heat) with a long flame of burning coal dust, blown in
 - a. Slag (fusible) formed from silica and alumina of ore with added CaCO_3
 - b. "Matte" of $\text{CuS} + \text{FeS}$ melts and is taken to converters
4. In converters hot air blast is blown through melted matte
 - a. Sulfur escapes as SO_2
 - b. FeS becomes Fe_2O_3
 - c. Fe_2O_3 reacts with silica and alumina of added raw ore to form slag, readily poured off
 - d. CuS becomes Cu (with a little Cu_2O)
5. Partial refining by repeating converter blowing

Reduction of Cu_2O by the action of reducing gases released from green wooden poles used as stirrers
6. Electrolytic refining; crude copper anodes dissolve as copper ions in bath of CuSO_4 and H_2SO_4 solution as fast as copper atoms are deposited on thin sheet of pure copper as cathode

Electrolytic Refining. Since the leading use of copper (as a conductor of electricity) demands a metal 99.95 per cent pure, it is necessary to remove all but traces of the arsenic, lead, silver,

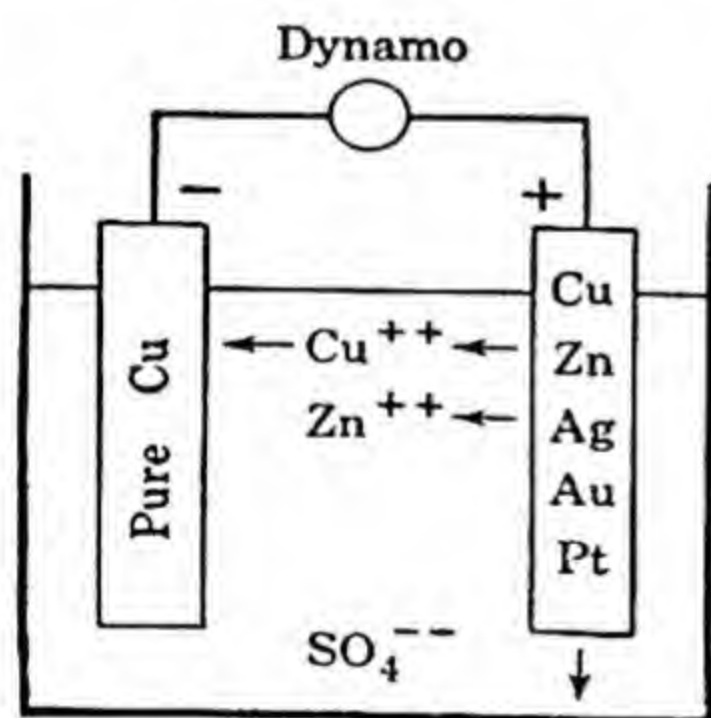


Fig. 138.

gold, and zinc impurities. As little as 0.01 of 1 per cent arsenic lowers the conductivity of copper about 5 per cent while 0.01 per cent of phosphorus lowers it 20 per cent. The slabs of cast copper from the smelters are made anodes in a bath of copper sulfate acidified with sulfuric acid. The cathodes are very thin sheets of pure copper arranged alternately with, and very close to, the anodes. The Cu^{++} ions are attracted to the cathode, where they are discharged

and deposited. An equal number of Cu^{++} ions are formed by the metal of the anode, passing into solution. The gold, silver, and platinum metals have less tendency to ionize, so they drop to the bottom of the huge vat as a mud mixed with other impurities. Any zinc or iron present in the anode

would ionize more readily than the copper and would deposit on the cathode if the Cu^{++} ions were not so much more easily discharged. Very little difference of potential between anode and cathode is needed, less than 0.5 volt, for discharge of Cu^{++} ions.

NICKEL

Occurrence and Preparation. Nickel occurs associated with arsenic or sulfur, or both, as in nicolite, NiAs , and nickel glance, NiAsS . Canada produced 88 per cent of the world's annual production of 200,000,000 pounds of nickel, or 176,000,000 pounds, in a recent year. New Caledonia, Burma, India, the Congo, and Cuba produced the rest. The Ontario ore is roasted and run through a Bessemer process. The "matte," or melted mixture of sulfides of nickel, copper, and iron, is "blown" until the iron is removed in the slag, leaving the sulfides of nickel and copper. There are two or three methods of separating the nickel from the copper.

By the Orford process some sodium sulfide is added to the melted matte of sulfides of nickel and copper. Two layers form, one of $\text{CuS} + \text{Na}_2\text{S}$ and the other of NiS . The nickel sulfide is roasted to convert it into the oxide which is then reduced, by hot carbon, to the metal.

An alloy of copper and nickel obtained from the Ontario ores is used as "monel metal," a tough, ductile alloy which resists corrosion. It can be cast and machines well.

MERCURY

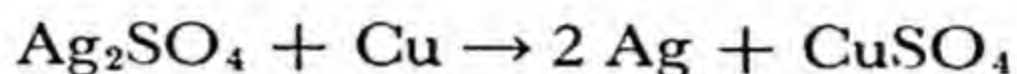
Occurrence and Metallurgy. To some extent it occurs free, but most of the world's mercury is obtained from the red sulfide, cinnabar, HgS . This is found in Italy, Spain, Austria, Mexico, the United States, and Japan. Of the world's production of 5000 tons the United States normally produces about one-sixth. The recent war emergency forced a large increase in our own production.

The sulfide ore is roasted in air and the volatile mercury condensed. Any mercuric oxide formed would be decomposed at the roasting temperature.

Occurrence. The principal ore of silver is argentite, Ag_2S , sometimes called silver glance. Lead and copper ores contain some silver, which is recovered in the refining processes. Mexico, the United States, Canada, and South America are all leading silver producers.

Metallurgy. When silver is cheap silver mines close down and the metal is mainly produced as a by-product of copper and lead refining.

The *leaching process* may be applied to the sulfide ores. Silver sulfide is roasted to form the sulfate, which is dissolved by water. Scrap copper added to the solution of silver sulfate displaces the silver and leaves copper sulfate as a valuable by-product:



Silver compounds are soluble in alkali cyanides, so silver ores may be leached with a solution of sodium cyanide. From this solution of the complex cyanide the silver is precipitated by the addition of zinc shavings.

By the Parkes process about 2 per cent of zinc is melted with silver-bearing lead. Since silver is far more soluble in zinc than in lead, and forms an alloy, Ag_2Zn_5 , it is taken up nearly completely by the zinc layer floating on top. As the mixture cools the zinc solidifies while the lead is still fluid. The zinc crust is removed and heated just hot enough to distill off the zinc, leaving a silver residue.

Recovery of silver from ores by the *amalgamation process* is discussed on page 523.

MOLYBDENUM

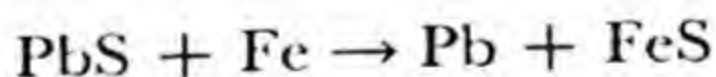
Molybdenum occurs chiefly as molybdenite, MoS_2 , a black lustrous mineral resembling graphite, but twice as heavy. Colorado operates the largest molybdenum property known and, with Arizona, produced 30,000,000 pounds of the world's 32,000,000 pounds a year. There is some ore in Mexico. The ore contains only one per cent of molybdenite, which is concentrated by the oil flotation process.

Roasting Sulfides with Carbon

LEAD

Occurrence. Like tin, lead was known to the ancient Egyptians because of the ease with which its ores are smelted. The Romans used lead pipes for water service. The sulfide, PbS, or galena, is the most important ore. Lead ores are common all over the world. In a normal year the United States produces 500,000 tons and imports much more. Mexico, Australia, and Spain produce smaller amounts, making a world production of more than 1,900,000 tons.

Metallurgy. Part of the lead sulfide ore is first roasted or sintered, forming a "matte" of mixed sulfides if copper sulfide is present. In the absence of copper sulfide roasting is continued until lead oxide is formed. This is then mixed with raw ore, coke, and limestone, and added to the furnace, where it meets a strong blast of air. The burning carbon and the carbon monoxide formed are both good reducing agents, as we have learned in connection with the smelting of iron ores. Lead oxide is reduced to the metal. The iron present as an impurity is burned to the oxide and, as we have seen in the study of the iron blast furnace, the oxide is reduced by hot carbon monoxide to the metal. But iron can extract sulfur from the raw lead sulfide, so in this case an impurity is a genuine aid:



The limestone carries off silica in the fusible slag, calcium silicate. A molten "matte" of iron sulfide with copper sulfide and some lead sulfide is separated to be treated for further extraction of lead.

Refining of lead usually involves the separation of antimony, arsenic, bismuth, and copper by oxidation. The lead is kept molten with stirring. These impurities oxidize more readily than lead and float to the surface as dross. Any gold or silver may be removed by Parkes' process (see Silver) or by Betts' electrolytic process. With electrolysis the impurities drop as anode mud (compare with purification of copper).

Electrolysis: Na, Ca, Ba, Mg, Al, Be

SODIUM

The preparation of metallic sodium by electrolysis of fused sodium hydroxide or sodium chloride has been discussed on page 206.

CALCIUM

Calcium is now made by electrolysis of the melted chloride in a carbon or iron cell with a graphite anode. The metal is molten when liberated and floats to the top of the bath, where it is chilled and slowly lifted out as a growing stick.

The crude calcium melts at 800° . Forty years ago the price was \$20.00 per pound but now the cost is less than \$1.00 for a metal 99 per cent pure.

Barium metal resembles calcium but has very little industrial use as yet. It has value in "getting" the vacuum in radio tubes, and in a high nickel alloy for auto ignition equipment.

Barium and calcium can also be prepared by reduction of their oxides with ferrosilicon at 2000° . This is similar to the Pidgeon process for magnesium.

MAGNESIUM

Magnesium is a very common element, although not a very cheap metal, because of the cost of its preparation. It occurs as magnesite, MgCO_3 , as the double salt, dolomite, $\text{MgCO}_3 \cdot \text{CaCO}_3$ and as the double chloride, carnallite, $\text{KCl} \cdot \text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$. Meerschaum is $\text{Mg}_2\text{Si}_3\text{O}_3 \cdot 2 \text{H}_2\text{O}$, and serpentine is $\text{Mg}_3\text{Si}_2\text{O}_7 \cdot 2 \text{H}_2\text{O}$. Soapstone, or talc, is $\text{Mg}_3\text{H}_2(\text{SiO}_3)_4$, and asbestos is $\text{CaMg}_3(\text{SiO}_3)_4$. Brucite is the hydroxide.

The United States has large deposits of the carbonate in Washington, Nevada, and California, of the hydroxide (brucite) in Nevada, and olivine (a silicate) in Washington. In Michigan the bromide and chloride occur in beds of common salt and, of course, the ocean is an inexhaustible source of the chloride.

Preparation. Davy (1808) isolated the metal in impure form by electrolysis (compare calcium), but Bussy prepared a co-

herent form in 1831 by reducing the chloride with metallic potassium. For a long time reduction with sodium was the commercial, but expensive, method of preparation.

The process in use now is the electrolysis of melted magnesium chloride to which have been added sodium chloride and potassium chloride to lower the melting point. In 1915 the metal cost \$5.00 per pound, and 88 pounds were made in this country, but the present cost of magnesium is about 20 cents per pound.

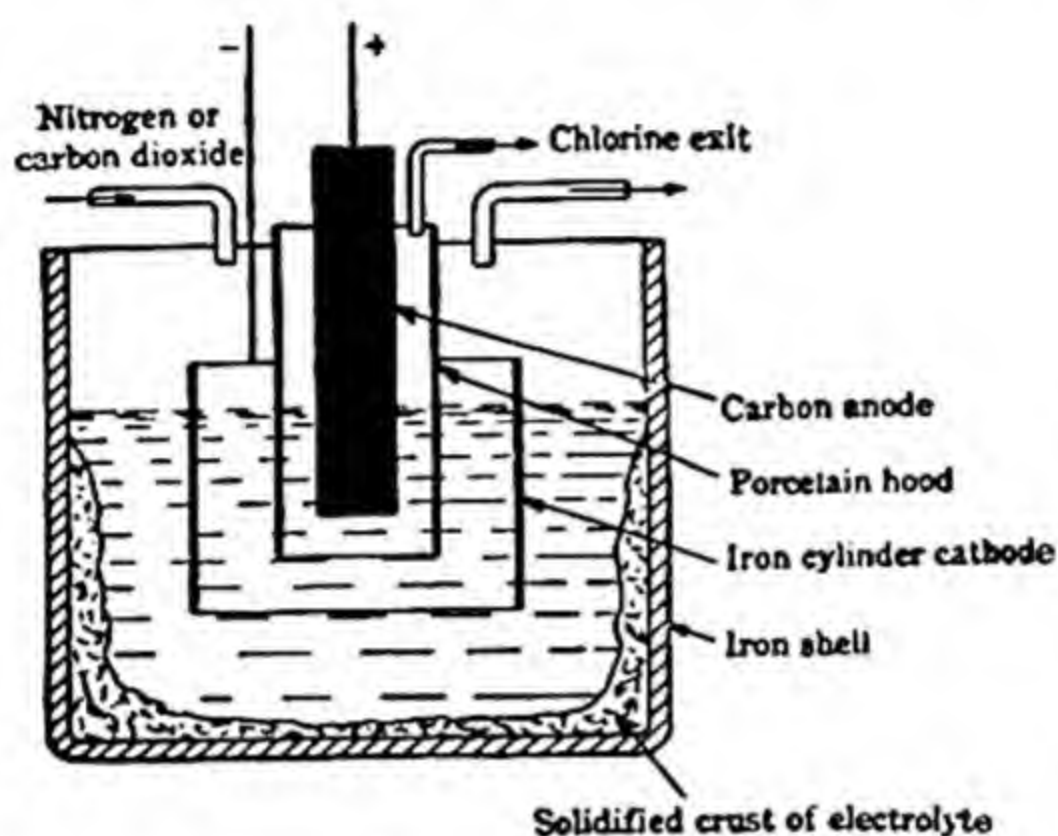


Fig. 139. Electrolytic preparation of magnesium.

One cubic mile of sea water contains 5,700,000 tons of magnesium, as chloride and sulfate. A huge plant now extracts magnesium metal from this unlimited reserve. Our production rose to 250,000 tons in 1944 but this was largely for military needs, aircraft and incendiary bombs. Only a small fraction of this total will be needed now.

Sea water is treated with lime to precipitate $\text{Mg}(\text{OH})_2$ which is then converted to MgCl_2 for electrolysis.

Exercises

1. The chloride for electrolysis has been obtained in one large plant by passing chlorine over hot magnesium carbonate and coal. Equations?
2. Addition of a slurry of lime to sea water precipitates the very insoluble magnesium hydroxide, readily converted into the chloride. How?

Although the heat of formation of magnesium oxide is very high, reduction of it with carbon in the electric furnace (air excluded) is possible. The metal vapor may be cooled to a powder on meeting a blast of cooled hydrogen or oil spray. Otherwise the reaction would reverse. This is the carbothermic process.

By the Pidgeon process silicon, as ferrosilicon, reduces magnesium oxide in a vacuum furnace (less than 1 mm. pressure). Magnesium vapor condenses in crystalline form. This was a war emergency process.

ALUMINUM

Occurrence. Aluminum is the most extensively distributed of the metals, making up about 7 per cent of the earth's crust. It never occurs free, but nearly all rocks except sandstone and limestone contain aluminum compounds. Such silicates as feldspar, KAlSi_3O_8 , and mica, KAlSiO_4 , are common. Ordinary clay, $\text{H}_2\text{Al}_2(\text{SiO}_4)_2 \cdot 2 \text{H}_2\text{O}$, cryolite, Na_3AlF_6 , bauxite, $\text{Al}_2\text{O}_3 \cdot 2 \text{H}_2\text{O}$, alunite, $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot \text{Al}_2\text{O}_3 \cdot 6 \text{H}_2\text{O}$, and corundum, Al_2O_3 , are well-known compounds of aluminum. Bauxite is the most important.

Preparation. Oersted, the Dane, was the first to isolate the metal (1825), yet for a century the world gave Wöhler the credit. The German changed Oersted's method slightly. Wöhler heated the anhydrous chloride with metallic potassium:



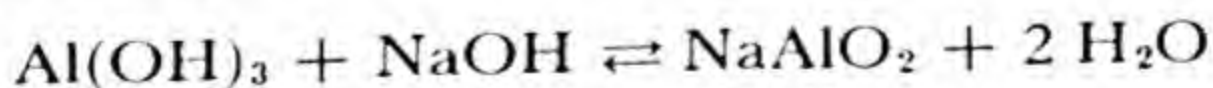
This method, yielding a metal that sold for \$160 per pound, (earlier in 1852 at \$545) was not destined to make aluminum compete with anything but museum specimens. The French chemist, Deville, improved the process in 1854 by using the cheaper sodium instead of potassium and the less volatile double chloride of sodium and aluminum instead of the simple chloride. The price fell rapidly from \$100 to \$17 in 1859 and two tons were produced. Castner, the American, attempted to cheapen aluminum by still further cheapening sodium and in this he succeeded in 1886. His work forced aluminum down to \$4 per pound.

Charles M. Hall, a student in Oberlin College, 1886, attacked the problem of making cheap aluminum and succeeded where the greatest scientists of the century had failed. It occurred to him that if he could find an easily melted mineral in which aluminum oxide dissolved, the solution might be electrolyzed. Such a mineral he found in cryolite, $3 \text{ NaF} \cdot \text{AlF}_3$, from Greenland. Hall secured his electric current from all the batteries he could borrow or make. By melting the cryolite in a graphite crucible with the heat of a charcoal furnace and using a carbon anode, he managed to secure a few buttons of the precious metal. By 1888 his company was producing aluminum commercially (Fig. 141). The price fell to 17 cents per pound in 1941 and to 15 cents in 1942.

Bauxite, $\text{Al}_2\text{O}_3 \cdot 3 \text{ H}_2\text{O}$, is found in several countries, notably France, the United States (Ark.), British and Dutch Guiana, and Hungary.

Most bauxite contains iron oxide as an impurity. This is removed by digesting the finely ground ore with concentrated sodium hydroxide under steam pressure, thus dissolving the aluminum as sodium aluminate without affecting the iron oxide.

Upon dilution, cooling, and "seeding" with a little freshly precipitated aluminum hydroxide, the sodium aluminate is hydrolyzed and the original aluminum hydroxide is reprecipitated:



The ignited hydroxide (now alumina, Al_2O_3) is added to the cell ready for electrolysis. These cells are iron boxes lined with a tarry material (retort coke). Several carbon anodes dip into the



Fig. 140. Charles M. Hall. Etching on aluminum.

bath, which is kept molten (about 1200°) merely by the heat of resistance. The carbon-lined iron cell is the cathode. The metal is discharged at the cathode and sinks to the bottom, to be tapped off from time to time. Oxygen is evolved at the anodes, possibly because fluorine is discharged at the anode and displaces oxygen from aluminum oxide. Since it is only the dissolved alumina that is decomposed, the cryolite should never need renewal — but it does. Calcium fluoride, aluminum fluoride, and the chlorides of

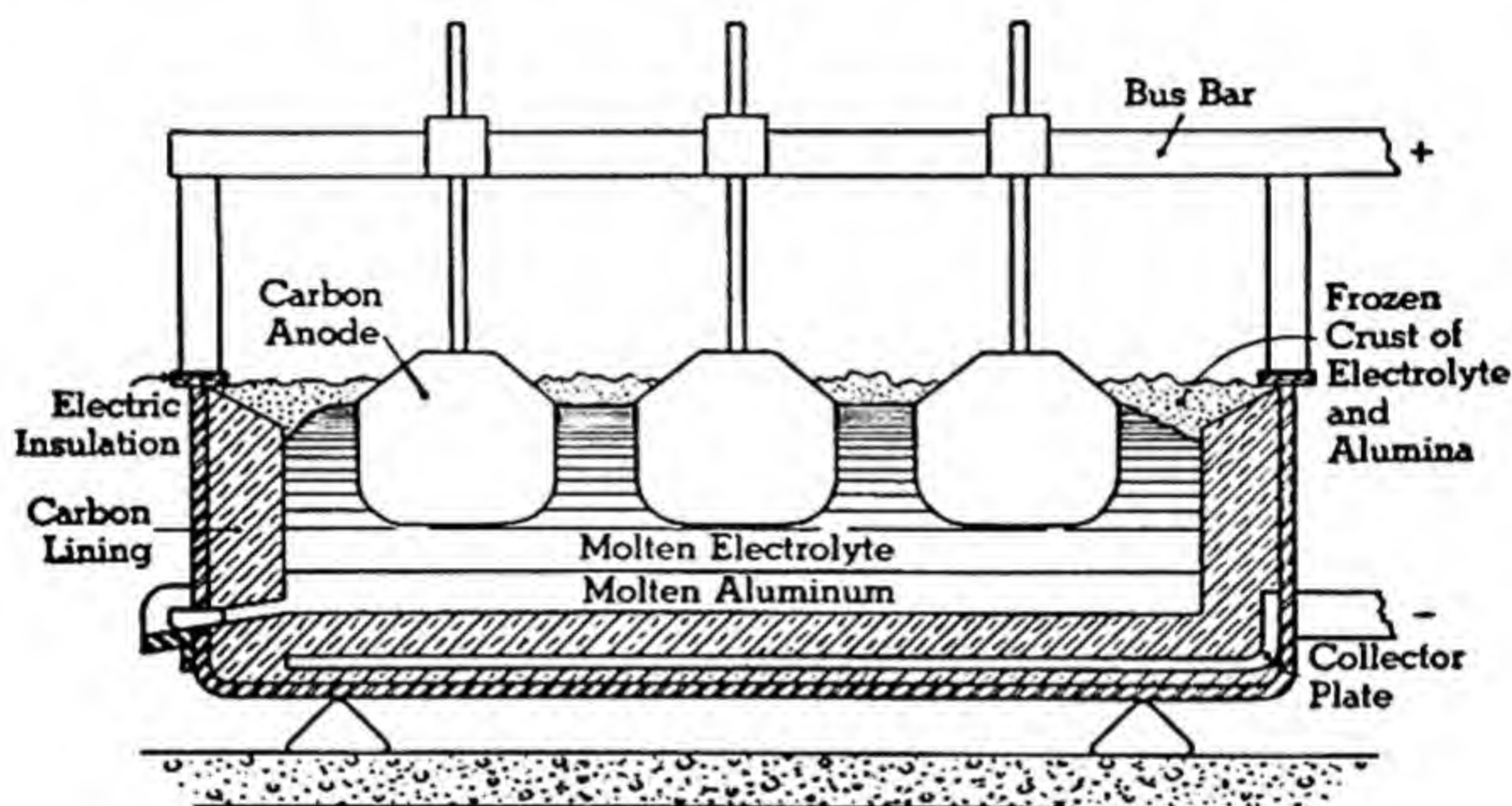


Fig. 141. Aluminum by electrolysis.

sodium, potassium, and aluminum are added in present practice to improve the bath. The potential fall in a cell is only about five volts, but a flow of several thousand amperes is maintained.

To make one pound of the metal, 2 pounds of aluminum oxide, 0.8 pound of carbon anodes, 0.1 pound of cryolite, 0.1 pound of fluorspar, and 12 KWH of electricity are required.

American production, because of war demands, rose in early 1944 to a yearly rate of 920,000 tons. Canada, Europe, and Japan also produced large tonnages. After the war our production fell, later rising sharply to 600,000 tons in 1948.

The American aluminum industry uses the excellent bauxite ores from the northern strip of South America and from Arkansas but it is possible, when these are exhausted, to make the metal

from a mixture of clay and bauxite, sintered with lime, and digested with soda to yield aluminum hydroxide. High silica bauxite, almost a clay, has been so treated. We also know how to treat the alunite ore of Utah.

BERYLLIUM

Beryllium, Be, occurs in the mineral beryl, a beryllium aluminum silicate of the formula $3 \text{ BeO} \cdot \text{Al}_2\text{O}_3 \cdot 6 \text{ SiO}_2$, and in aquamarine. When the former is transparent and tinted green with chromium silicate, it is called emerald. Wöhler prepared the element in 1828 by heating the chloride with potassium.

To prepare the amphoteric hydroxide, $\text{Be}(\text{OH})_2$, from the ores, a new process calls for quenching the hot ore in water, then sulfuric acid. The sulfate so formed is dissolved and then precipitated as the hydroxide to be converted into the oxide, BeO . The oxide is reduced with carbon in the electric furnace in the presence of copper which alloys with the beryllium. Or a fused bath of BeCl_2 and NaCl may be electrolyzed.

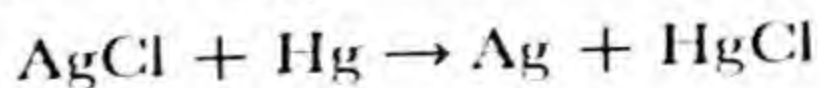
In this country a master alloy of about 3 per cent beryllium with 97 per cent copper is sold to be alloyed with other metals.

Amalgamation with Mercury

SILVER

Occurrence. Silver ores were discussed on page 516 and methods of extracting the metal (except the amalgamation process) were explained.

Metallurgy. The *amalgamation process* is applicable to ores carrying free silver, or to silver chloride. By roasting the sulfide ores with sodium chloride, they yield silver chloride, which can then be amalgamated. Crushed ores treated with mercury yield an amalgam of silver-mercury. This is separated from the waste rock and distilled in an iron retort. The volatile mercury is condensed for further use and the silver is left in the retort. Silver chloride with mercury yields metallic silver by simple displacement and the excess mercury then amalgamates it:



The Cyanide Process: Ag, Au

SILVER

Silver compounds are soluble in alkali cyanides, so ores may be leached with a solution of sodium cyanide. From this solution of the complex cyanide the silver is precipitated by the addition of zinc shavings.

GOLD

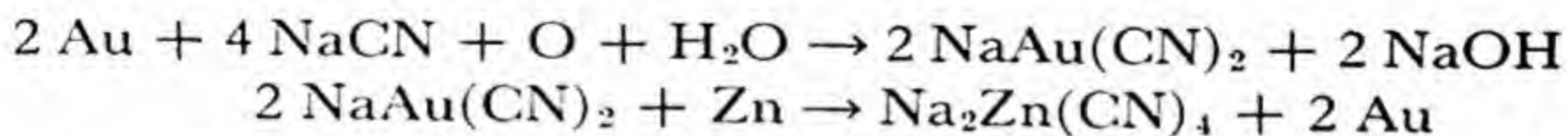
Gold occurs free or alloyed with silver. Its only compound found in nature is the telluride, AuTe.

The Transvaal of South Africa leads in production with the United States in second place, and Australia and Russia follow in that order.

Since Columbus discovered America a billion ounces of gold have been mined — equivalent to a golden cube 41 feet on edge — 60 per cent of it produced in the first 35 years of this present century.

Quartz rock carrying veins of gold is crushed and the material washed over cleats of amalgamated copper. The gold amalgam formed is worked up like the silver amalgam previously described.

In the cyanide process low-grade ores are leached in presence of air with sodium cyanide solution to form the soluble sodium auro-cyanide from which the gold is secured by displacement with zinc or by electrolysis:



(The platinum metals are discussed on page 550.)

Powder Metallurgy

Metals of high melting point, such as tungsten, molybdenum, and tantalum, which cannot be melted and cast are prepared in mass by powder metallurgy with the aid of heat and pressure. Even with metals of lower melting point there are a number of advantages in the use of powder metallurgy such as omitting the

usual final machining and grinding of small and complicated articles. The metal powders are prepared by reduction of oxides or by atomization. Metals which are immiscible in the melted state or which are widely different in volatility may be alloyed readily by sintering, but not melting, their mixed powders.

Hard carbides, cemented by cobalt, are shaped by powder metallurgy for cutting and grinding tools.

Exercises

3. Is magnesium made by any other method than electrolysis?
4. What is a "matte" in metallurgy?
5. What new idea in the metallurgy of aluminum did Hall contribute?

References

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Chapter 47 PROPERTIES AND USES OF THE METALS. PART I

The properties of a metal dictate its uses. For strength we use steel (modified iron); for great chemical resistance platinum is preferred; while for ductility and electrical conductivity copper meets the great commercial demands.

METALS

1. Form basic hydroxides
2. Form simple positive ions
3. Reflect light well when polished
4. Conduct electricity and heat well
5. As a class are malleable and ductile

NON-METALS

1. Form acidic hydroxides
2. Do not form simple positive ions
3. Do not usually show "metallic luster"
4. Do not conduct heat and electricity well
5. In general are not malleable or ductile

This is an historical classification to be used with several qualifications. For example, there are a few elements such as zinc and aluminum whose hydroxides yield both hydrogen ions and hydroxide ions in water. Furthermore the higher-valence number hydroxides of manganese, chromium, and lead are acidic, while their lower-valence number hydroxides are basic.

Metallic properties are usually associated with few valence electrons — four or less.

In metallic crystals the valence electrons are not tied to any particular atom but exist as a kind of free electron gas.

A preliminary classification of metals by properties should be much more interesting than a mere encyclopedic recital. Ten properties are used for classification below, although others could be added — expansion on heating, for example. In fact cast iron has added value because it expands on solidifying to fill the mold sharply.

1. The Light Metals. Although sodium, potassium, and lithium have low specific gravities there are only two metals, aluminum and magnesium, used because they possess low densities (Al, 2.7; Mg, 1.74).

2. The Most Active Metals. The alkali metals (Na, K, Li, Cs, Rb) as a class are the most active chemically and have laboratory interest for that reason. Commercially we find it convenient to use the reasonably active calcium or barium as “getters” in cleaning out the gases in vacuum tubes after pumps have done their best. These metals are active enough to react with both nitrogen and oxygen of the air. Calcium will deoxidize certain molten metals, as will hot aluminum. In fact the useful thermit process (page 510) depends upon the activity of hot aluminum to steal oxygen from some other metallic oxides.

3. The Least Active Metals. At the lower end of the activity series of metals are the “noble metals,” so lazy chemically that they are commercially useful because of that property. Platinum and its group are invaluable for laboratory crucibles, and for dental and jewelry uses. Compact protective films of oxides make aluminum and some other metals seem less active. Copper, too, tarnishes with a green coating of the basic carbonate, yet the metal beneath lasts for centuries. Even lead, although tarnished in air, has considerable permanence if not in contact with acetic or nitric acids.

4. Corrosion-Resistant Metals. The “noble metals” just mentioned might be included here although for chemical equipment copper and silver would have limitations — they are attacked by nitric and certain other acids. Tantalum, also, is highly resistant to attack.

A few metals that resist atmospheric corrosion (unlike common steel) are useful as protective coatings, and are deposited by dip-

ping in the melted metal, by spraying melted metal, or by electroplating. Tin-plated steel, galvanized iron or steel (zinc coating), nickel and cobalt plating, silver plating, aluminum coating, and chromium plating are all of commercial importance.

At high operating temperatures (as in the cracking tubes of petroleum refineries) chrome-steel alloys or chromium-plated steels are required. Phosphate-coated steel is rust-resistant.

5. Low-Melting Metals. It is very convenient in thermometers, barometers, pressure gauges, and various types of scientific apparatus to use a liquid metal such as mercury.

Fortunately for the plumber, for workers in type metal and solders, and for other technicians, lead melts at 327.5° , a low temperature compared with copper's 1083° . At the opposite extreme it is fortunate that tungsten has a high melting point, for as a filament in some electric lamps it may reach a temperature of 2500° . It melts at 3370° .

6. Metals Readily Volatilized. The mercury-vapor lamp and the sodium-vapor lamp (giving us excellent illumination where used on highways) are possible because of the ready volatility of these metals. Recovery of mercury from its amalgams with gold and silver (secured in metallurgy of their ores) depends upon the great differences in boiling point of the metals concerned. The use of boiling mercury in one type of high vacuum pump is well known. Recovery of zinc from ores heated with coke depends upon the ease with which zinc volatilizes.

Metal wires, rapidly heated in a high vacuum by an electric current, are vaporized and deposited on solid surfaces by a process called "sputtering." It has been found that the atoms in such films arrange themselves evenly in layers 50 atoms deep, in the shapes of the metal crystals underlying them, and not according to their own crystal lattice. The deposited film is gripped hard by every atom in the surface beneath.

7. Ductile and Malleable Metals. The more ductile metals, such as gold, silver, copper, and aluminum, belong to the face-centered cubic lattice type. Less ductile metals, such as molybdenum, tungsten, and chromium, belong to the body-centered

lattice type, in which the face-centered atoms of the unit cube are replaced by a single atom at the cube center.

Columbium and tantalum are extremely ductile and may be worked cold.

As a costly stunt aluminum was recently drawn into a wire $\frac{1}{25}$ th the thickness of the average human hair.

Iron can be rolled into suitable shapes when red hot. Zinc is most readily rolled at 100° – 150° and is almost brittle at 205° . Gold leaf has been hammered to a thickness of 0.0001 mm. Lead is far from ductile, although malleable, while platinum wire has been drawn to a diameter of 0.00008 mm., and 1 gram of gold can be drawn into a wire 3240 meters in length.

8. Strong Metals. When great tensile strength is required we usually turn to alloys such as steel, yet a tungsten wire (drawn) has the extremely high tensile strength of 600,000 pounds per square inch cross section. The values for hard drawn iron (100,000 pounds), nickel wire (155,000 pounds), and tin (5000 pounds) are interesting in comparison.

For great strength we usually use impure metals (alloy steels).

9. Metals of High Electrical Conductivity. Silver, under certain conditions, is the best conductor but copper is second and is also plentiful, so it dominates the electrical industry. For cables transmitting electrical power aluminum (although the cable must be thicker than a copper cable) is a rival. Platinum and mercury have laboratory uses which depend on their conductivity.

10. Highly Colored Metals. It is remarkable that of all the metals only gold and copper have decided color. Their alloys (brass, bronze, etc.) may also have color. This property adds to their commercial value.

NORMAL PRICES

Tin	46 cents per lb.	Lead	5 cents per lb.
Nickel	35	Zinc	4.5
Magnesium	20.5	Steel	2.8
Aluminum	15	Pig iron	1
Copper	15		

THE ALKALI METALS

ELEMENT		ATOMIC WEIGHT	DENSITY g./ml.	MELTING POINT	BOILING POINT	ATOMIC VOLUME = $\frac{\text{AT. WT.}}{\text{DENSITY}}$
Lithium	(Li)	6.94	0.534	186.0°	1200.0°	13.1
Sodium	(Na)	23.997	0.971	97.5°	880.0°	23.7
Potassium	(K)	39.096	0.862	62.3°	760.0°	45.4
Rubidium	(Rb)	85.48	1.532	38.5°	700.0°	55.8
Cesium	(Cs)	132.91	1.90	28.5°	670.0°	71.0

This group of elements, as shown by its position in the periodic system, is strongly metallic. The alkali metals are the most active of all metals, reacting violently with water, and hence are not found free in nature. In the laboratory these metals must be kept under oil to exclude moisture and oxygen. Their hydroxides are the strongest bases. The elements are soft with a silvery luster, and quickly tarnish in the air with the formation of layers of oxide, hydroxide, and carbonate. All the elements of this group are obtained by electrolysis of their fused salts or hydroxides. The valence number is uniformly one throughout the group.

Metallic lithium is so active that it reacts slowly with dry nitrogen at room temperatures. As a scavenger in purifying molten metals it reacts with nearly all the non-metallic impurities and gases present.

Lithium vapor, by uniting with oxygen of the air, furnishes a reducing atmosphere for welding, heat treating, and carburization of metals. In such an atmosphere no black oxide, Fe_3O_4 , can form on hot steel.

Cesium is the most active of all metals and is used in photo-electric cells for its sensitivity to light. It is coming into use as the vapor in a vacuum tube rectifier, changing alternating into direct current.

Metallic sodium is shipped in forty-ton tank cars, and is loaded and unloaded in the molten condition. Since it is important in the manufacture of sodium cyanide (so much used in electroplating and in heat treatment of metals), of sodium peroxide, of indigo, of tetraethyl lead used as an anti-knock agent in gasoline, and of sulfapyridine, there is a rather large demand for this active metal.

Sodium-cooled valves are used in the most powerful airplane motors.

THE ALKALINE-EARTH METALS

ELEMENT	ATOMIC WEIGHT	DENSITY g./ml.	MELTING POINT	VALENCE NUMBER
Beryllium (Be)	9.02	1.73	1300°	2
Magnesium (Mg)	24.32	1.74	651°	2
Calcium (Ca)	40.08	1.55	810°	2
Strontium (Sr)	87.63	2.54	800°	2
Barium (Ba)	137.36	3.75	850°	2
Radium (Ra)	226.05	5.0	960°	2

BERYLLIUM

Properties. Beryllium is a brittle light-gray metal, capable of taking a high polish, hard enough to scratch glass, four times as elastic as aluminum but only two-thirds as heavy, and almost as elastic as steel. Chemically it resembles aluminum and alloys with it; but in the free state it looks like crystalline silicon. Its density is about 1.73 g./ml. and its melting point 1300° C., near which temperature it oxidizes readily in the air.

In 1922 it sold (a few grams of it) at \$5000 per pound; now it may be had at \$15 or less per pound, in master alloys with copper or nickel.

The outstanding property of beryllium is its high elasticity. Springs of beryllium nickel alloys possess marvelous resistance to fatigue.

To copper and iron it adds hardness; but it does not alloy at all with magnesium. The alloys with iron, copper, and nickel are improved by heat-treatments.

As a window in X-ray tubes beryllium transmits the rays seventeen times as well as the usual aluminum window.

MAGNESIUM

Properties. Magnesium is a silvery white metal melting at 651° and boiling at 1100°. Its low density of 1.74 g./ml. is interesting, for there is only one other commercial possibility, aluminum, among the light and strong metals to compete with it as an en-

gineering material, and aluminum has a density of 2.70. It is important commercially that magnesium does not rust in dry air. A thin film of hydroxide, turning into the basic carbonate, does form in moist air, but it is coherent enough to protect the metal beneath. At a temperature just below its melting point the metal can be drawn into wire.

Magnesium of 99.99 per cent purity can be prepared by sublimation of the crude metal below its melting point of 651° , under reduced pressure (2 mm. of mercury). The vapor condenses in a beautiful crystalline mass.

One of the chief uses of magnesium is in alloys with aluminum, which may contain from 8 to 25 per cent magnesium. They are harder, lighter, stronger, and more easily machined than aluminum alone.

Chemically, magnesium is a rather active element, since it displaces hydrogen from boiling water. It also has some value in organic syntheses. Magnesium unites with most non-metals. With nitrogen it forms the nitride, Mg_3N_2 , of interest because it reacts with water to form ammonia. Magnesium burns at 600° with a brilliant white light, strong in actinic rays, hence its use in flashlight powders. It is much used in star shells for military illumination. Magnesium is not attacked by strong bases while aluminum is, but on the other hand magnesium is attacked by weak acids.

Although powdered magnesium burns brilliantly the metal can be hot forged in the form of bars.

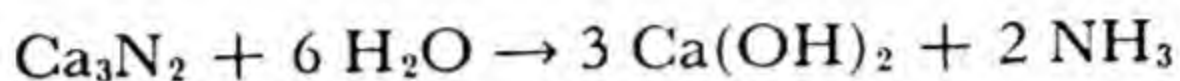
War demands (incendiary bombs and aircraft) increased our magnesium production in 1943 to fully 100 times the 1939 production.

Radium was treated in earlier chapters but it belongs in this group. The metals of this group are like the alkalies in that they form rather strong bases.

All the elements are divalent in their compounds. All are active, displacing hydrogen from cold water with moderate speed. They are silvery white metals when freshly cut, but quickly tarnish in air because of formation of the oxides and probably the carbonates. They are somewhat harder than lead.

CALCIUM

Properties. Calcium is a silver-white metal, melting at 810° . Its density is 1.55 g./ml. The metal can be rolled and drawn. When hot it can be worked much more easily, but oxidation increases rapidly with rise in temperature. The hot metal unites readily with both oxygen and nitrogen; hence it can be used in securing a vacuum. Its nitride yields ammonia in contact with water:



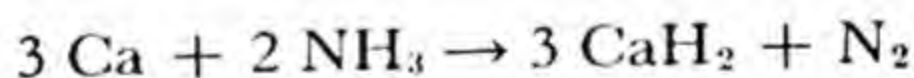
Calcium metal is growing in favor as a deoxidizer of copper and steels, a lead hardener (particularly for lead cables and bearing metals), in aluminum alloys, as an agent in reducing the oxides of beryllium and chromium, as a desulfurizer in oil refining, and as an absorbent of residual gas in radio tubes.

Only 0.25 per cent of calcium in magnesium alloys improves tensile strength and ductility.

A storage-battery grid of Pb-Ca instead of the usual Pb-Sb gives longer life to the battery.

A bearing metal of Ca-Ba-Pb is made by electrolysis of the fused chlorides of calcium and barium over a molten lead cathode.

Calcium removes bismuth and other impurities from lead. With ammonia it reacts in a strange way:



BARIUM AND STRONTIUM

The properties of barium and strontium are similar to those of calcium. Only the barium has any use, as a "getter" in vacuum tubes.

COPPER, SILVER, AND GOLD

	ATOMIC WEIGHT	DENSITY	MELTING POINT	VALENCE NUMBER
Copper (Cu)	63.57	8.92	1083°	2(1)
Silver (Ag)	107.88	10.5	960.5°	1
Gold (Au)	197.2	19.3	1063°	3(1)

Compared with the other family (Na, etc.) of Group I of the Periodic Table, copper, silver, and gold are much harder, far heavier; and all three melt near 1000° . They are so inactive they do not react with water and, in fact, do not displace hydrogen from acids. Copper forms a very thin film of oxide in air, but gold and silver are not affected by air. This inactivity explains the occurrence of these three metals free in nature. Consequently they were known in ancient times. Their beauty made them especially desirable.

COPPER

Properties. Copper is red by reflected light, but greenish by transmitted light. The two colors may be observed with thin sheets such as "Dutch foil." Copper melts at 1083° and boils at about 2310° . The melting point in air is lowered about 20° by the oxide formed, which is soluble in copper. The metal has a density of 8.92 g./ml. It is remarkably malleable and ductile, and when annealed is the best of the cheaper metals as an electrical conductor but when drawn into wire it is second. If it lacked either in ductility or conductivity, there would not be much copper wire on the market.

Oxidizing acids attack copper and even acetic acid will, slowly, attack the oxide film formed from the action of air.

The green coating acquired by copper roofing and bronze statues outdoors was once thought to be the basic carbonate. In cities it contains the basic carbonate but near the sea it contains some basic chloride.

Uses. Copper wire in the electrical industry, copper alloys, copper roofing, copper electrotypes call for 1,000,000 tons of this metal in a normal year in the United States.

SILVER

Properties. Silver is a white metal melting at 960.5° in the absence of air. In the air it melts at 955° , due to the fact that 22 volumes of oxygen dissolve in one volume of molten silver, thus lowering the freezing point. On cooling, this oxygen escapes with a curious spattering of the surface crust. Silver is the best conductor of electricity and but for its cost would displace copper

from the electrical industry. Silver is remarkably ductile, having been drawn to wire so fine that 1800 meters weighed 30 g. It is so malleable that foil has been prepared 0.00025 mm. in thickness. It boils at 1950° and has a density of 10.5 g./ml.

Chemically, silver is inactive. It is not affected by hot oxygen, but it slowly reacts with sulfur and the halogens. Silver spoons become tarnished with a layer of sulfide especially when in contact with eggs.

Uses. Cheaper objects are electroplated with silver by making them the cathodes in a bath of the double cyanide. The plated surface has a frosted appearance until polished. Silver plating only one-millionth of an inch thick has been deposited on copper and steel. Practically all mirrors are now made by reducing an ammoniacal solution of silver nitrate with glucose, formaldehyde, or Rochelle salts. The reduced silver is deposited on glass and is then varnished to protect it. In earlier days tin amalgam formed the reflecting surface. Silver is much used in coinage, ornaments, and in the preparation of its halogen salts for the photographic industry. One-third of all the silver produced in the United States is used to make silver bromide for this industry.

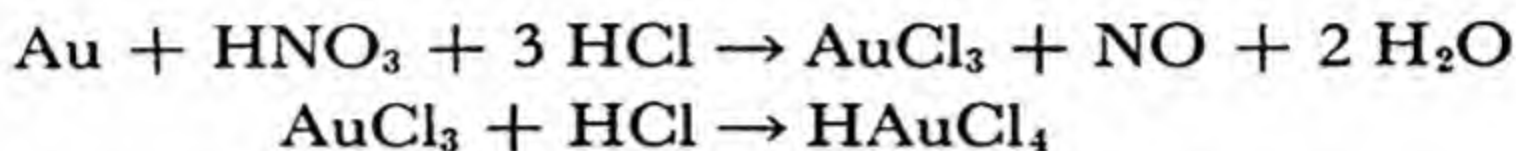
A leading manufacturer of picture film and plates uses more than 2000 tons of silver every year.

The United States Treasury hoards 100,000 tons of silver but during World War II it loaned about 15,000 tons to be used as heavy bus bars in electrolytic industries, to replace copper.

GOLD

Properties. Gold leads the metals in ductility and malleability. Gold leaf has been hammered so thin that it required 110,000 sheets to reach a total thickness of 1 cm. Gold wire has been drawn so fine that 3240 meters weighed only one gram. Gold melts at 1063° and boils at 2600° . It is too soft to be used pure, so coins and jewelry contain copper as a hardening agent. United States gold coins were 90 per cent gold. In jewelry the purity of gold is rated by carats of fineness. Pure gold is 24 carats fine, while the usual jewelry alloy of 18 carats is only 18/24 pure. The specific gravity of pure gold is high, 19.3.

Chemically, gold is inactive. Not only is it indifferent to oxygen and hydrogen sulfide, but it resists the attack of nitric acid. However, free chlorine slowly attacks it. Consequently the mixture of concentrated nitric and hydrochloric acids (containing some nitrosyl chloride and free chlorine) called *aqua regia* dissolves gold, forming auric chloride, which, with excess of hydrochloric acid, forms chlorauric acid:



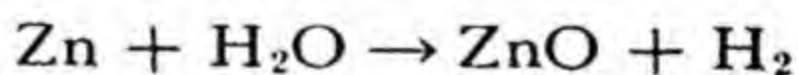
Although the world produces 1000 tons yearly 90 per cent of it is hoarded in government gold reserves.

ZINC, CADMIUM AND MERCURY

		ATOMIC WEIGHT	DENSITY g./ml.	MELTING POINT	VALENCE NUMBER
Zinc	(Zn)	65.38	7.14	419°	2
Cadmium	(Cd)	112.41	8.65	320.9°	2
Mercury	(Hg)	200.61	13.546	-38.87°	2, 1

ZINC

Properties. Zinc is a blue-white metal whose properties vary with its treatment. Cast zinc is moderately hard and brittle, but if heated to 100°–150° it becomes so malleable that it can be rolled to thin sheets, which remain soft and malleable on cooling to ordinary temperatures. The melting point is sometimes given as 419.4°, but varies above or below this according to the physical history of the sample. Zinc tarnishes in air with the formation of a film of basic carbonate. When very hot it reacts with steam:



It burns in air with a bluish flame and the formation of white fumes of the oxide. It is the most active of the cheap metals, so it is made the “dissolving element” of most primary cells, yet pure zinc scarcely is attacked by dilute sulfuric acid. The presence of another metal or impurity, less active, causes a rapid attack of the zinc by the acid, although the bubbles of hydrogen are released on the surface of the other metal. Zinc dust particles are usually

covered with a film of oxide. On exposure to moist air large quantities of zinc dust in storage have been known to take fire.

Uses. The most important use of the metal is in the galvanizing of iron to protect the iron from rusting. As zinc itself does not rust, the iron beneath cannot be attacked until the zinc surface is scratched or broken.

Galvanizing is done by cleaning the rust or scale from iron with dilute sulfuric acid and dipping the clean iron into melted zinc. On cooling, the zinc crystallizes in the familiar spangled design. At least 2 oz. per square foot of surface are needed to give protection.

Rolled zinc is used for roofing, gutters, washing-machine parts, and battery elements. Alloyed with copper it forms brass, one of the most useful of all alloys. Zinc dust is a valuable reducing agent in organic syntheses. Zinc salts are poisonous, so food containers should not be made from this metal.

Zinc of 99.99 per cent purity is remarkably ductile and brilliant and may be used to coat wire or sheet steel. Melted zinc can be sprayed on steel as a coating. It also yields better die castings than the less pure metal.

CADMIUM

Properties. Cadmium looks much like zinc, melts at 320.9° , boils at 770° , and has a density of 8.65 g./ml. Its chief use has been in low-melting alloys, such as those used for automatic fire sprinklers and electric fuse wires. Some cadmium is also used for special solders and bearing metals. In recent years alloys of cadmium with nickel or silver or copper have come into extensive use as bearing alloys for high-speed machinery. The bearing is often plated with indium. Its use is growing rapidly in several important alloys, as a white foundation for silver plating, and as a rival to nickel plate. Production in the United States is 4,000,000 pounds per year.

MERCURY

Properties. Mercury is a beautiful silvery liquid at ordinary temperatures, in fact it is the only metal liquid under such con-

ditions. Cesium and gallium come near it. Mercury freezes at -38.87° , boils at 356.9° , and has a high density, 13.546 g./ml. at 0° . When heated well above its boiling point, the vapor conducts electricity quite well with radiation of a bluish-green light rich in ultra-violet rays. Lamps using this principle are made of glass tubes when only the visible light is desired, but when the ultra-violet rays are wanted for water sterilization or other purposes, the tube must be of clear quartz. Glass stops ultra-violet rays, while quartz lets them through.

Mercury is used in thermometers, air pumps, gas-measuring and collecting apparatus, and was once essential to the manufacture of mirrors. Now all mirrors have a silver reflecting surface. Mercury forms amalgams with many metals.

Chemically, mercury is almost a "noble" metal. It is oxidized slowly by air only above 300° , as Lavoisier learned in his classic experiment (page 39). Mercury is not attacked by any acids except with oxidizing ones, such as nitric and hot concentrated sulfuric acid. The metal is not poisonous in the mass, but some of its soluble salts are, as is its vapor.

The mercury-vapor turbine produces more power than the corresponding steam turbine but 155 tons of mercury were required for one large installation.

Exercises

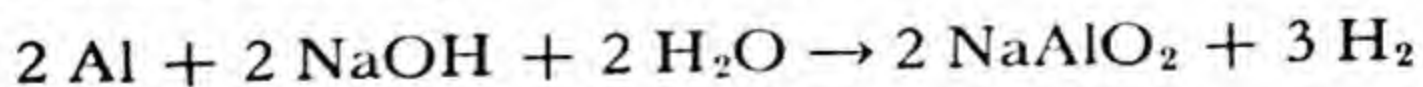
1. What are the three light metals suited to engineering work?
2. What are the uses of magnesite, MgCO_3 ?
3. What metals might substitute for copper, if it ceased to exist?
4. Of what use is calcium?
5. Why do we want ductile metals?
6. What metal, or alloy, makes springs that are never fatigued?

Chapter 48 PROPERTIES AND USES OF THE METALS. PART II

ALUMINUM

Properties. Aluminum is one of the lightest of the very common metals, its density being only 2.7 g./ml. (iron is three times as heavy). In color it somewhat resembles silver, but has a bluish sheen. It melts at 660° and boils at 1800°. It is rolled or hammered most easily at 100°–150°. Near the melting point it is so brittle that it can be ground to flakes, in the presence of a lubricant. It is an excellent conductor of heat and electricity. In wire of the same cross section and equal length it conducts electricity only two-thirds as well as copper, but weight for weight it excels copper in this respect. More than 500,000 miles of steel-cored aluminum cables are in use. Only iron and copper among the common pure metals have greater tensile strength.

Chemically aluminum is very active, yet it is tarnished only slightly in air. This is because of the formation of a thin coherent film of the oxide which protects the metal beneath. Sometimes it is desirable to thicken this oxide film by anodic oxidation in a bath of sulfuric or dichromic acid. Hydrochloric acid dissolves aluminum readily with the escape of hydrogen, but cold dilute nitric acid attacks it hardly at all. This is probably due to the oxidizing action of nitric acid. Like zinc this metal is dissolved by solutions of sodium or potassium hydroxide:



Commercial aluminum is 99.2 per cent pure (the remaining percentage made up of iron and silicon). Cold rolling increases the strength. Cooking utensils contain 1.25 per cent manganese. Some 600 million aluminum cooking vessels have been made in this country.

A smooth, bright surface of aluminum is a splendid reflector of radiant heat and consequently the metal deserves its growing use as a heat insulator for locomotives, milk tanks, houses, and naval vessels. Naturally the foil is just as efficient as heavy sheets and is lighter. On a locomotive 13 pounds of such foil can replace 1200 pounds of other insulating material.

Reflecting mirrors for telescopes were formerly coated with silver but now they all probably will be coated with metallic aluminum which is a far better reflector of the invisible ultra-violet rays from stars. This is no help to the eye but photographic films can "see farther" into space with the aid of such reflection. Such aluminum coatings (especially if underlaid by a coat of chromium) are hard enough to stand gentle polishing and resistant enough to require replacement but rarely — a great advantage over silver coatings.

Pure Aluminum. Success in rolling thin layers of pure aluminum on sheets of duralumin has added greatly to the usefulness of this strong alloy.

Uses of Aluminum. Because it is light, strong, and not noticeably corroded in air, aluminum has many commercial uses. It is now used in large quantities to remove air bubbles from steel ingots at the moment of pouring. The light aluminum oxide formed floats to the top. Aluminum is much used for auto parts, the rigid structure of airships, and structural work of various kinds. The powdered metal is mixed with oil or a volatile liquid and used as a paint for radiators and other metallic articles. Aluminum paint is largely used as a covering for oil storage tanks in order to reflect much of the sun's heat radiation and thus lessen the usual losses of volatile constituents such as gasoline. Since its salts are not poisonous the thin foil is used as a food wrapper.

Molten aluminum, sprayed on common steel prevents formation of black oxide, Fe_3O_4 , when such steel is heated in air. The golden bronze containing 92 per cent copper and 8 per cent

aluminum is now much used for gears in auto trucks and for other purposes where toughness, and resistance to abrasion and corrosion are important. Some modern alloys of this type have the advantages of strength approaching that of steel, great hardness, resistance to corrosion, beauty, susceptibility to high polish, and lightness. Finally, such bronzes can be cast readily while steel is cast with difficulty. In all probability the greatest future of

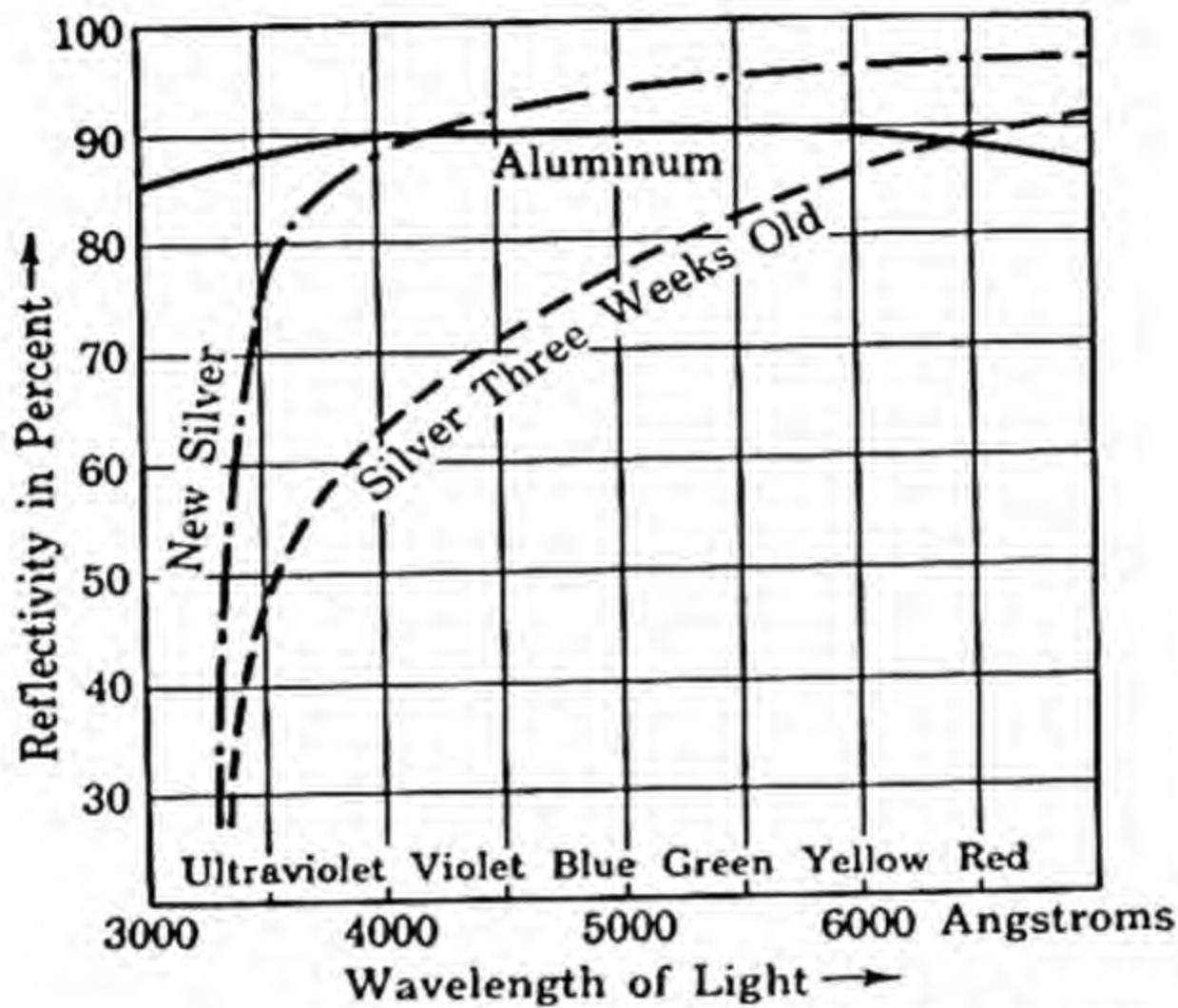


Fig. 142. An aluminum coating is the best surface for the concave mirror of the reflecting telescope.

aluminum lies in the direction of alloy making. Street cars and furniture are now being made from aluminum or its alloys. Architectural parts such as grills, roofing and window frames, auto pistons, containers (even collapsible tubes) provide a large market for this metal. Aluminum plated with nickel or chromium is now in use. Why?

Competition

Processes to make:

Hall electrolytic

Remelted scrap

ALUMINUM

In competition with:

Steel

Copper

Magnesium

Tin (cans)

Bronze

Wood

Duralumin, the greatest of all aluminum alloys, containing 95.5 per cent aluminum, 3 per cent copper, 1 per cent manganese, and 0.5 per cent magnesium, is much used in airplane, airship, and auto construction. It has the strength of steel with

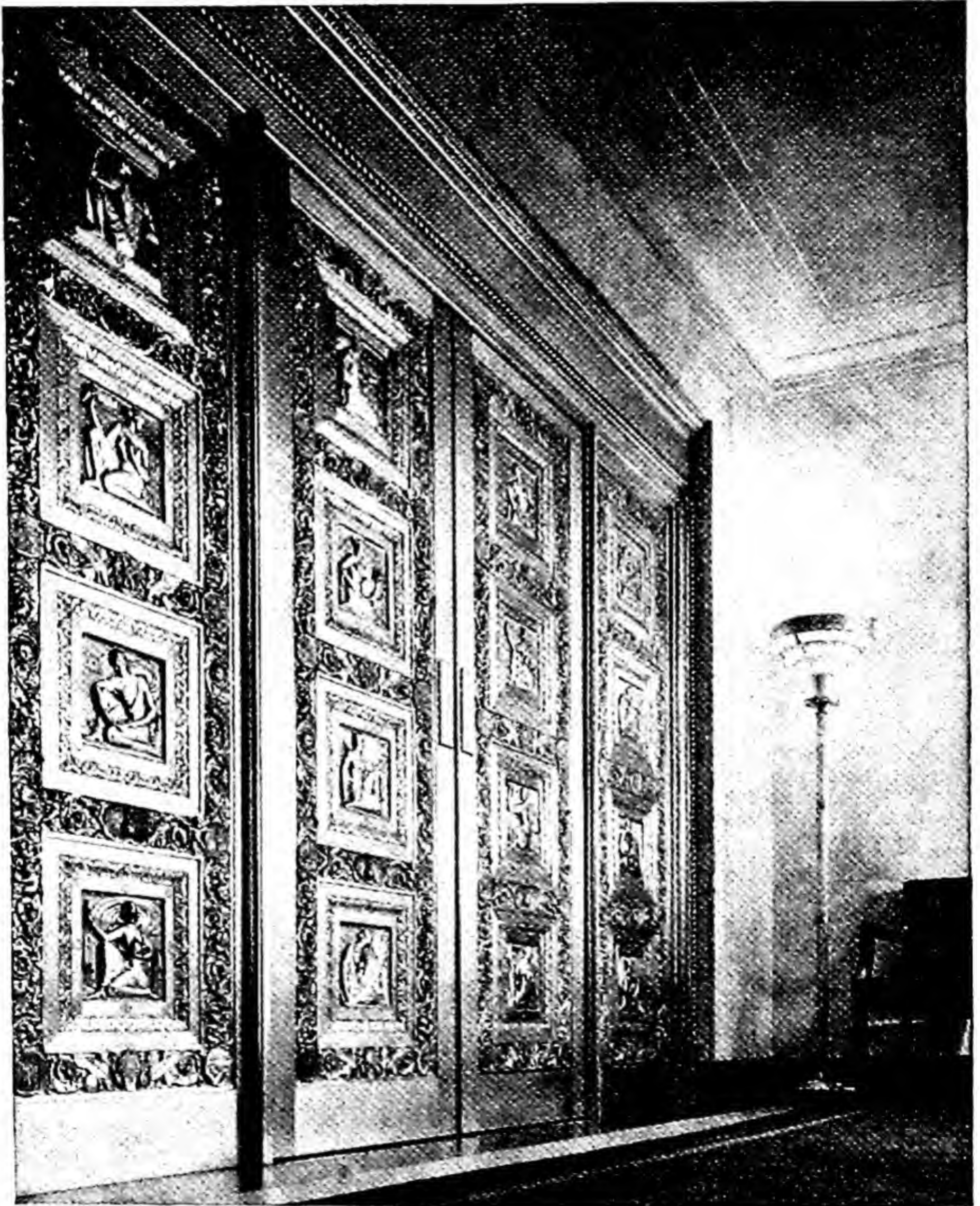


Fig. 143. Magnificent doors of cast aluminum in the Pittsburgh offices of the Aluminum Company of America.

about one-third of its weight. Heat-treatment of aluminum alloys greatly improves them. A very recent alloy, "755," strongest in its class, contains about 90 per cent aluminum, some magnesium and zinc, and traces of a few other elements.

Gallium and *Indium*, belonging to the aluminum family, show some promise of future uses. Gallium melts at 30° .

"In seventy-five years *indium* has evolved from a pair of spectrum lines to a metal available in commercial quantities." It occurs as an impurity in zinc ores and production could be increased to two tons yearly at 40 cents an ounce. Its vapor in a vacuum tube can radiate red light.

Can you suggest possible uses for this metal, soft enough to be cut with a knife, very malleable, melting in the flame of a match, lustrous as silver, unattacked by air or water, alloying with silver, platinum, and certain other metals?

For example, it is now added to certain dental alloys to increase hardness, toughness, and tarnish resistance. Indium, electroplated on a base metal, alloys with the base beneath on heating and can later be polished to a brilliant finish. Indium surfaced bearings and propellor blades are in use on planes.

The *rare-earth* metals have little use except in the familiar pyrophoric mixture on a gas lighter. Their compounds are more important.

TIN AND LEAD

	ATOMIC WEIGHT	DENSITY g./ml.	MELTING POINT	VALENCE NUMBER
Tin (Sn)	118.7	7.31	231.85°	2, 4
Pb (Pb)	207.21	11.337	327.5°	2, 4

TIN

Properties. Tin is a white metal melting at 231.85° and boiling at 2260° . Its density is 7.3 g./ml.

Tin is most malleable at 100° , while at 200° it is so brittle that it can be ground to a powder. (What other metals become brittle when heated?)

Tin is plated on thin sheets of iron or steel by mere dipping of the clean steel into melted tin or by electroplating. The sheet must first be pickled in acid to free it from all oxides of iron. The

modern ideal in tin plating is to secure as thin a coating of tin as possible, 1.25 per cent of the total weight, without holes or cracks. From such tinned sheets are made common tin cans, cups, pails, pans, and a hundred cheap and useful articles. The manufacture of 19,000,000,000 tin cans yearly in this country provides one of the large markets for steel. Our dependence upon tin was evident to all when this country was cut off from the East Indies.

War shortages of tin forced the development of electroplating of a moving sheet of metal (steel) followed by a quick flash of electric induction heating to melt the tin so it would fill up all pinholes. For such tin plate only one-third as much tin is needed as was used by previous methods.

Chemically, tin is not very active. It is affected neither by the moisture nor by the carbonic acid of air and does not readily tarnish. It is these properties that make it so useful. In acids the metal dissolves slowly. Dilute nitric acid converts it into stannous nitrate, $\text{Sn}(\text{NO}_3)_2$, without the evolution of hydrogen. Somewhat concentrated nitric acid converts tin into an insoluble oxide, SnO_2 . Dry chlorine attacks the metal much more readily than it does iron, so tin scrap may be treated with chlorine to obtain tin chloride. Hot concentrated sulfuric acid converts tin into stannic sulfate, $\text{Sn}(\text{SO}_4)_2$.

LEAD

Properties. Lead is a heavy metal of specific gravity 11.337, soft, and easily cut with a knife. The metal melts at 327.5° and boils at 1620° . Just below its ordinary melting point (lowered by pressure) it can be squeezed into tubes. When freshly cut, its luster is bright, but the surface quickly tarnishes with formation of oxide and basic carbonate. This coating protects the metal from further oxidation, although it detracts sadly from the real beauty of lead.

Chemically lead does not always seem as active as it is. For example, cold hydrochloric acid scarcely attacks it. Lead chloride forms a protective coating over the lead. Hot acid dissolves this and permits the metal to be attacked. Lead sulfate, too, is insoluble and has a protecting action. But when above 80 per cent

in concentration, sulfuric acid dissolves lead sulfate and consumes the metal. Nitric acid dissolves lead with release of oxides of nitrogen rather than of hydrogen. Acetic acid slowly attacks lead in the air, due to the preliminary oxidation of the metal and subsequent reaction of the oxide with the acid. This reaction is fundamental in the manufacture of white-lead paints.

A very small intake of lead by man is usual, due to insecticides sprayed on fruits, traces in vegetables, lead oxide in the auto exhaust, food contact with certain enamels and, for a million workers, lead hazards in industry. The U. S. Public Health Service considers 0.36 part of lead in a million parts of water to be toxic.

toxic.

Lead	{	Bearing metal		
		Type metal		
		Storage-battery plates		
		Solders		
		Expansion bolts attaching iron to stone		
		Toys		
		Electric fuses		
		Collapsible tubes		
		Lead pipe		
		Sheet lead		
		Cable covering		
		Lead foil		
Lead Compounds	{	Paint Industry	{	White lead
				Red lead
				Orange mineral
				Chrome yellow
				Basic lead sulfates
		Glass, Pottery Industry	{	White lead
				Red lead
				Litharge
		Rubber Industry	{	White lead
				Basic lead sulfate
		Match Industry	{	Litharge
				Red lead
		Storage-Battery Industry	{	Lead peroxide
				Red lead
		Linoleum Industry	{	Litharge
Same compounds				
as in				
Paint Industry				
Textile Industry	{	Lead nitrate		
		Lead acetate		
Medicine	{	Litharge		
		Lead acetate		
Insecticides	{	Lead acetate		
		Lead arsenate		

Solutions of lead salts are extremely poisonous, so that water conducted through lead pipes may produce lead poisoning. This is particularly true of soft water, which with air forms the somewhat soluble $\text{Pb}(\text{OH})_2$. Hard water is much less dangerous because it soon forms a coating of insoluble carbonate and sulfate on the lead. Therefore, a bright lead pipe is under suspicion. The worst feature of lead poisoning is that it is cumulative. Traces of lead may be taken into the body for years, and a fraction remains.

Although lead is attacked by alkali, a very little sodium silicate in the alkaline solution protects lead pipes so exposed.

Uses. Lead is the cheapest metal other than iron. Its resistance to the attack of moist air and of several acids makes it useful in lining vats or tanks. Sulfuric acid chambers are lined with it, water pipes are made of it (by forcing lead through holes under a pressure of 33 tons per square inch), and common shot are formed from it. Solder is an alloy of lead and tin; Babbitt (anti-friction bearing metal) is a lead alloy; type metal contains it; and some collapsible metal-tube containers for pastes are lead alloys. Storage batteries use antimony-lead plates and all lead paints begin with lead as raw material.

A lead-sodium alloy is used in the manufacture of tetraethyl lead to be added to gasoline as an anti-knock agent.

Terne plate for roofing is made by dipping clean steel sheets into a molten lead containing 10–20 per cent of tin. Without the tin, lead fails to coat steel dipped into it.

The largest uses are for storage batteries, cable sheathing and the manufacture of tetraethyl lead.

GROUPS VIA AND VIIA

		ATOMIC WEIGHT	DENSITY mg./ml.	MELTING POINT	VALENCE NUMBER
	Chromium (Cr)	52.81	7.1	1615	2, 3, 6
(VIIA)	Manganese (Mn)	54.93	7.2	1266	2, 3, 4, 6, 7
	Molybdenum (Mo)	95.95	10.2	2620°	2, 3, 4, 5, 6
	Tungsten (W)	183.92	19.3	3370°	2, 3, 4, 5, 6
	Uranium (U)	238.07	18.7	1400°	3, 4, 5, 6

Chromium and Manganese

CHROMIUM

It is difficult to overstate the importance of chromium among the metals. Alone it is of no great importance but in various alloys it is a key metal. Chromium in alloy steels increases hardness and strength without sacrificing toughness or ductility.

Chromium is a brilliant, silvery metal, hard and brittle, melting at 1615° and showing a density of 7.1 g./ml. The powdered metal burns in oxygen with formation of the trioxide, Cr_2O_3 . With chlorine it forms the chloride, as it does with hydrochloric acid. In fact, it is easily attacked by cold concentrated or hot dilute hydrochloric and sulfuric acids. Yet nitric acid does not affect the metal.

Chromium is now attracting the attention of many manufacturers. The value of chromium as a metal in its own right lies in (1) its great hardness and hence its suitability for printing-plates, dies, gauges, cams, and gears, (2) its high luster and resistance to tarnish, which render it useful for exposed reflectors, and (3) its resistance to atmospheric corrosion. These properties led the way to chromium plating (usually over nickel plating) on automobile radiator shells, bumper bars, plumbing fixtures, petroleum pressure cracking stills, and other objects.

Chromium fails to tarnish in air because of a thin film of protective oxide which, however, readily dissolves in concentrated hydrochloric acid.

MANGANESE

Manganese is a reddish-gray metal melting at 1266° . It boils at 1900° but it may be distilled in a high vacuum at a much lower temperature. It has a density of 7.2 g./ml. It is very brittle and hard enough to scratch glass. In the air it is not tarnished, but acids as weak as acetic attack it. Its use in alloy steels is important.

Vanadium, Molybdenum, Tungsten, and Uranium

The very great importance of vanadium, molybdenum, and tungsten as alloying elements in special steels is discussed on pages 566 and 567.

VANADIUM

The element is silvery white, very hard, and rather brittle. It melts at 1710° and has a density of 5.96 g./ml.

MOLYBDENUM

The free element, as prepared by the aluminothermic process, is silvery white, melts at 2620° , and has a density of 10.2 g./ml. Ferro-molybdenum is the form in which this element is added to steel.

Molybdenum is indispensable in vacuum tubes and in all electrical equipment where high conductivity and great strength and rigidity at high temperatures are needed.

TUNGSTEN

Tungsten has the highest melting point of all the metals, 3370° . Only carbon has a high melting point, but carbon at high temperatures has a greater vapor pressure than tungsten. Tungsten is steel-gray, very hard, and very heavy, with a density of 19.3 g./ml. The metal is obtained as a powder, on reduction of the oxide, and is worked into strong filaments or rods. Tungsten-steel cutting tools can operate at high temperatures without losing hardness.

Tungsten carbide (W_2C), with some cobalt, was developed in 1928 as the hardest cutting-tool material yet manufactured ("*carbology*").

Tungsten lamp filaments are saving the people of this country nearly three billion dollars each year. The old carbon filaments used 3.25 watts per candle power, while the modern tungsten lamp uses less than 1.25 watts for the same illumination. We use more than 900,000,000 of these lamps annually.

URANIUM

Uranium is a white metal, melting at about 1400° . Its density of 18.7 g./ml. ranks it as one of the heaviest elements. It slowly oxidizes in the air and dissolves in the common acids.

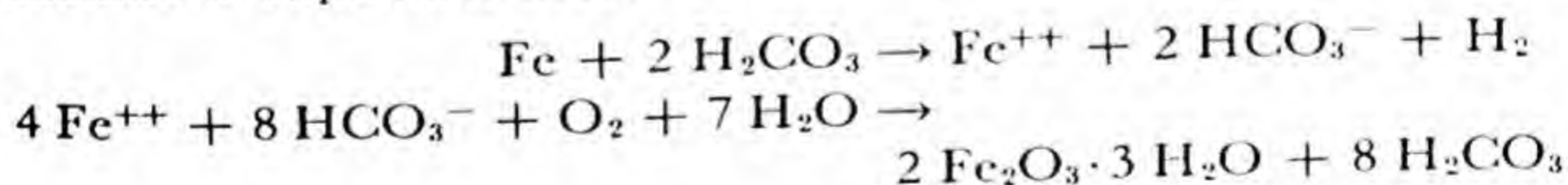
IRON, COBALT, AND NICKEL

	ATOMIC WEIGHT	DENSITY g./ml.	MELTING POINT	VALENCE NUMBER
Iron (Fe)	55.84	7.86	1535°	2, 3
Cobalt (Co)	58.94	8.9	1480°	2, 3, (4)
Nickel (Ni)	58.69	8.9	1452°	2, 3, (4)

IRON

Properties of Pure Iron. A single outstanding property of iron — magnetism — made possible the dynamo, motor, compass, telegraph, telephone, and other invaluable servants of mankind. The pure element has a density of 7.86 g./ml. and is very ductile and malleable. It melts at about 1535° . It is not hardened by sudden cooling like steel. Chemically it is rather active, rapidly displacing hydrogen from acids. It **rusts** slowly in water and air, displacing hydrogen. Weak acids, even carbonic, hasten this greatly. Consequently bases inhibit rusting. In moist air the metal rusts rapidly with formation of $2 \text{Fe}_2\text{O}_3 \cdot 3 \text{H}_2\text{O}$ as a loose, soft scale.

The chemistry of rusting in air containing moisture and carbon dioxide is explained below:



The element iron crystallizes in the body-centered lattice at room temperature and has a face-centered cubic allotropic modification above 900°C . Alpha iron (ferrite) is the chief component of wrought iron. It is soft, ductile, and magnetic. Gamma iron, stable only above 910° , is denser and only slightly magnetic. Pure iron, because of its quick magnetic change, is used for the armatures of dynamos.

Crude iron (pig or cast iron) is hard and brittle because of carbon and other impurities. It is discussed under "Metals" on pages 505 and 506.

COBALT

Properties. The metal is hard and white like iron, yet it is also malleable and ductile. It melts at 1480° and has a density of 8.9 g./ml. It displaces hydrogen slowly from ordinary dilute acids, but is readily attacked by nitric acid. It forms remarkable acid-resisting alloys with some metals, and one new alloy is used for exhaust valves of planes. Cobalt is used as a binder in carbide tools.

NICKEL

Properties. Nickel is a white, magnetic metal resembling iron. It melts at 1452° and has a density of 8.9 g./ml. It is hard, malleable, takes a high polish, and does not tarnish readily in the air.

Although this metal has extensive use as a protective coating electroplated on steel, its greatest service is in "stainless steel" and other alloys. (See page 567.)

An alloy ("permalloy") of 80 per cent nickel and 20 per cent iron with traces of other metals shows extraordinary magnetic permeability after receiving a special heat-treatment. Its initial permeability is more than thirty times that of soft iron; consequently it is now used for submarine cables, permitting four times the former speed of cabling. The copper cable is wrapped spirally with a narrow tape of permalloy with gutta percha outside. "Alnico" is an alloy of Ni-Al-Co-Fe which can be given permanent magnetism sufficient to lift sixty times its weight of iron.

THE PLATINUM METALS

	ATOMIC WEIGHT	DENSITY g./ml.	MELTING POINT	OXIDES
Ruthenium	101.7	12.3	2450°	RuO , Ru_2O_3 , RuO_2 , RuO_4
Rhodium	102.9	12.5	1955°	RhO , Rh_2O_3 , RhO_2
Palladium	106.7	12.	1555°	PdO , PdO_2
Osmium	190.2	22.5	2700°	OsO , Os_2O_3 , OsO_2 , OsO_4
Iridium	193.1	22.41	2350°	Ir_2O_3 , IrO_2
Platinum	195.23	21.45	1755°	PtO , PtO_2

The platinum metals are rare and are found usually as the free elements. Canada now leads in production, with Colombia, South Africa, the United States, and Russia also producing. World tonnage of platinum is 600,000 ounces, half of it from Canada.

The nobility of these metals decreases in the order, $\text{Ir} > \text{Ru} > \text{Rh} > \text{Pt} > \text{Os} > \text{Pd}$. The first three resist boiling aqua regia. Platinum will resist any single mineral acid.

Complex chloro-acids of the type H_2PdCl_4 , etc., are known for all these metals.

PLATINUM

It is unfortunate that this element is so rare, for it is most useful. It has been worth more than five times as much as gold, but now is on a par with gold. Its high melting point, 1755° , its resistance to chemical corrosion, and its remarkable powers as a catalyst make it almost indispensable. In the laboratory it is used in the form of crucibles, wire, and sheet. Certain precautions must be taken in its use, as it is attacked by chlorine and aqua regia as well as by fused alkalis. It also alloys with a number of easily reducible metals. When hot it is permeable to hydrogen, so that easily reduced compounds of certain metals should not be heated in platinum dishes over a gas flame.

Platinum has been the best metal for electric wire "lead-ins" through glass because of its coefficient of expansion and its good adhesion to glass. Now a cheaper tube of copper (filled with a nickel-iron alloy of lower coefficient of expansion than glass) has been developed. Copper is wetted better by molten glass and adheres better than any other metal. It is easy to weld platinum at a red heat and in general it may be classed as rather malleable and ductile. It also conducts electricity moderately well although a Pt-Ir alloy is better. Platinum is attacked by aqua regia with the formation of H_2PtCl_6 .

When ammonium chloroplatinate, $(\text{NH}_4)_2\text{PtCl}_6$, is ignited, a finely divided form of the metal called *platinum sponge* is secured. Asbestos soaked in chloroplatinic acid and heated yields the metal in fine particles scattered through the asbestos. Such forms

of platinum are used as catalysts in various industries, notably in the contact process of making sulfuric acid. The Ostwald process for oxidizing ammonia to nitric acid uses platinum gauze, covered with reduced platinum in a spongy form, or alloyed with rhodium.

Tantalum, rarer than gold and chemically resistant, is finding many new uses. Its melting point is exceeded only by that of tungsten. It is attacked only by hydrofluoric and hot, concentrated sulfuric acids. It is already used in spinnerets, electronic tubes, and as a catalyst. Its carbide is extraordinarily hard, and its alloy with tungsten is hard enough to be used for fountain pen tips.

Plates of tantalum (strong and malleable) are excellent for the repair of skull injuries, and its wire form has been used in suturing nerves. This element is discussed here only because it competes with platinum. Tantalum melts at 2856° and has a density of 16.6 g./ml.

PALLADIUM

Palladium is associated with platinum in the natural alloys and resembles it in appearance and some properties. Yet it is more like silver in that nitric acid dissolves it; then, too, it is softer, lighter, and melts more easily than platinum. Palladium's most interesting property is its ability, when finely divided, to absorb 800 volumes of hydrogen — 900 volumes if a strip of the metal is made the cathode of an electrolytic cell. Palladium possesses such great resistance to the attack of oxygen, moisture, and hydrogen sulfide that it is sometimes used for the inner mechanism of watches, for fine balance beams, surgical instruments, and special apparatus. It is used in soldering platinum, as a catalyst and, alloyed with ruthenium, in jewelry. Only palladium in this group is attacked by nitric acid. The metal is hardened by five per cent of ruthenium.

RHODIUM

Rhodium is not attacked by aqua regia or any acid, but reacts with chlorine. A 0.0001-mm. layer of rhodium protects silver from tarnish — and it can be plated on. There are two chlorides, RhCl_2 and RhCl_3 . Three oxides are known: RhO , Rh_2O_3 , and RhO_2 . Rhodium is harder than platinum. A little rhodium alloyed with platinum improves that metal as a catalyst for the

oxidation of ammonia. Plated on jewelry this blue-white metal is hard and corrosion-resistant.

Upon fusion with KHSO_4 rhodium is converted into the soluble sulfate. Platinum-rhodium spinnerets are used in spinning viscose rayon.

IRIDIUM

This element resembles rhodium in its resistance to aqua regia. Since it is very hard and not oxidized at high temperatures it is useful for some apparatus and in the preparation of iridium-osmium alloy tips for fountain pens. Although iridium sells at about \$55 per ounce, we import 4000 ounces annually.

There is an increasing use by jewelers of iridium as a hardening agent for platinum.

OSMIUM

Osmium is remarkable in having the greatest density, 22.5 g./ml., of any substance known. It is gray like iron, but, unlike that metal, resists the attack of aqua regia. However, it unites easily with oxygen when heated, forming the poisonous tetroxide, OsO_4 , wrongly called "osmic acid."

CRUDE NATURAL PLATINUM

Pt	79.5%	Os	0.3%
Ir	6.2%	Ru	0.008%
Pd	2.6%	Au	0.6%
Rh	0.6%	Cu. Fe	10.12%

Exercises

1. Compare the metallurgy of copper and iron.
2. Why not secure metallic aluminum and magnesium by electrolysis of aqueous solutions of their salts?
3. Advantages of the aluminothermic method of preparing certain metals?
4. Importance of the new electrolytic method of preparing manganese from low-grade ores?
5. Name one good ore of each metal.
6. The heat of combustion of calcium is greater (per gram equivalent) than the heat of combustion of aluminum. Could you reduce CaO to metallic calcium by the thermit process?

7. Classify the following metals in four groups as to cost: Cheap, moderately priced, rather expensive, costly.
Iron, copper, lead, radium, tin, silver, aluminum, magnesium, sodium, mercury, tungsten, vanadium, molybdenum, beryllium, manganese, chromium, cesium.
8. Suppose you wished to extract the metal from a metallic oxide with a heat of formation of 2500 calories. Would you decompose it by heat, reduce with hot hydrogen, or electrolyze its solution in some melted salts (as Hall did with aluminum oxide)?
9. What properties make chromium useful in plating steel or copper?
10. Give a few illustrations of the competition between metals in industry. For example, how does aluminum compete with steel? With copper?
11. What metals count in military power?
12. What are the uses of metallic calcium?
13. Why is molybdenum important?
14. For what uses are ductile metals valuable? Extremely hard metals (or alloys)?
15. Chart the air and acid resistance of fifteen different metals.
16. What is the influence of carborundum, tungsten, and molybdenum on machine-shop work?
17. Plot density of metals (Appendix) against atomic numbers. Do you see any relation of a periodic type?
18. Beryllium-alloy tools are non-sparking. Of what importance is this?
19. What metals are useful in the electrical industry? Why?
20. Why is a platinum-iridium alloy used for the tips of fountain pens?
21. How recover aluminum from scrap containing steel?
22. What are the surgical uses of tantalum?

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Chapter 49 ALLOYS. STEEL

Alloys were invented in attempts to improve upon the properties of the metals. In ancient times copper and zinc were alloyed to form brass, and copper was alloyed with tin to form bronze. Alloys have multiplied greatly in number, but it is only recently that their preparation and study have become genuinely scientific. Here is a field of dazzling promise, only partly explored as yet. Over 9000 alloys are listed in a recent book.

Metals of nearly the same atomic radius usually dissolve in each other when melted together, to form a solid solution when cold.

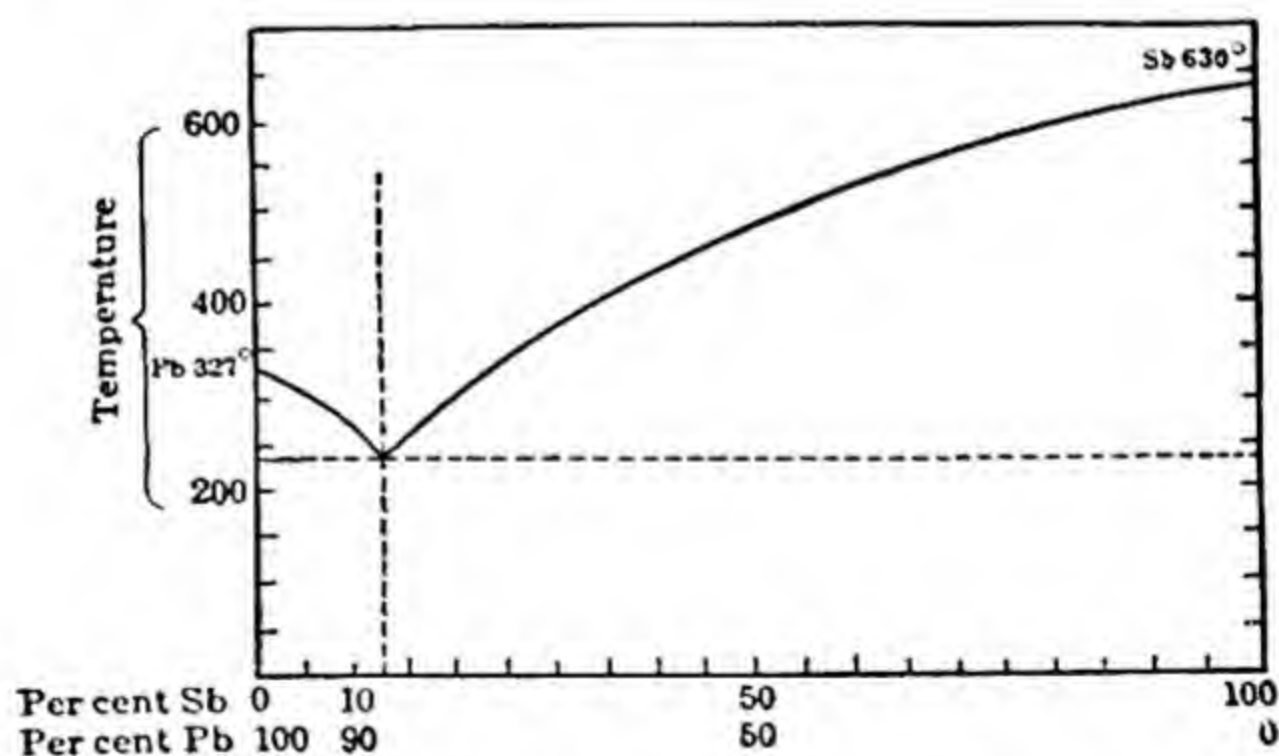


Fig. 144. Melting-point curves of varying mixtures of lead and antimony.

Eutectic Alloys. Lead melts at 327.5°C. , but when antimony is dissolved in the molten metal the freezing point of the lead is lowered, just as the freezing point of water is lowered by dissolved substances. Antimony melts at 630.5°C. and the addition of lead to melted antimony also lowers its freezing point. If a curve is

drawn showing the temperature where the lead just commences to solidify (or the temperature of its complete melting) as antimony is added, and if from the other side of the diagram a similar curve is drawn showing the lowering of the freezing temperature of the antimony as lead is added, these two curves will meet in a point, and the temperature and the composition represented by this point on the diagram will indicate the melting point and percentage composition of the lowest-melting alloy of the series.

This lowest-melting alloy represented by the point *E* has a definite melting point (248° C.) and a definite composition (87.5 per cent lead) and is called the *eutectic* of the series.

Mixtures of melted salts show the eutectic phenomenon. For example lithium chloride melts at about 600° C. and potassium chloride at 800° C. but their eutectic mixture melts at approximately 350° C. With other proportions of the salts the melting point is higher than 350° C.

A eutectic mixture of 88 per cent gold and 12 per cent germanium melts at 356° although the elements separately melt at 1063° and 989° . This alloy is harder than gold, and expands slightly on cooling.

Types of Alloys. Alloys are of at least four main types:

1. A solid solution of one metal in another, or in several others
2. A definite chemical compound of two or more metals
3. A mixture of such a compound with an excess of either constituent — this means particles of the compound are in a matrix of the rest of the material
4. A mixture of a solid solution with an excess of either constituent

In some bearing metals hard intermetallic compounds such as Cu_3Sn are dispersed in a softer eutectic such as Cu-Sb-Sn.

Alloys are usually made by melting the constituents together, although they can be made in other ways. On cooling, solid particles of one type may separate from the uniform molten mixture. When a polished surface of such an alloy is etched by a suitable chemical and examined under the microscope, the shape and arrangement of these crystals or aggregates are clearly seen and may be photographed. Such a study is called "metallography."

Microscopic examination shows that metals and alloys are rather complex in structure, that they are built up of aggregates of crystalline grains. The strength and other physical properties of alloys depend to a marked extent on the size and arrangement of these grains.

Intermetallic compounds do not conform to ordinary valence expectations. For example, Hg_2Na , BiTe , AuSn , and AuMg_3 are not reconcilable with the valences of the elements, yet compounds with these formulas are very stable. X-ray study shows that Cu_5Zn_8 is right and Cu_2Zn_3 wrong.

Intermetallic compounds form most readily between atoms which have but one or two outermost electrons and atoms with five or six in the outermost level. Such compounds are hard and brittle and conduct heat and electricity poorly.

If a metal and a non-metal yield a product with metallic properties it is called an alloy.

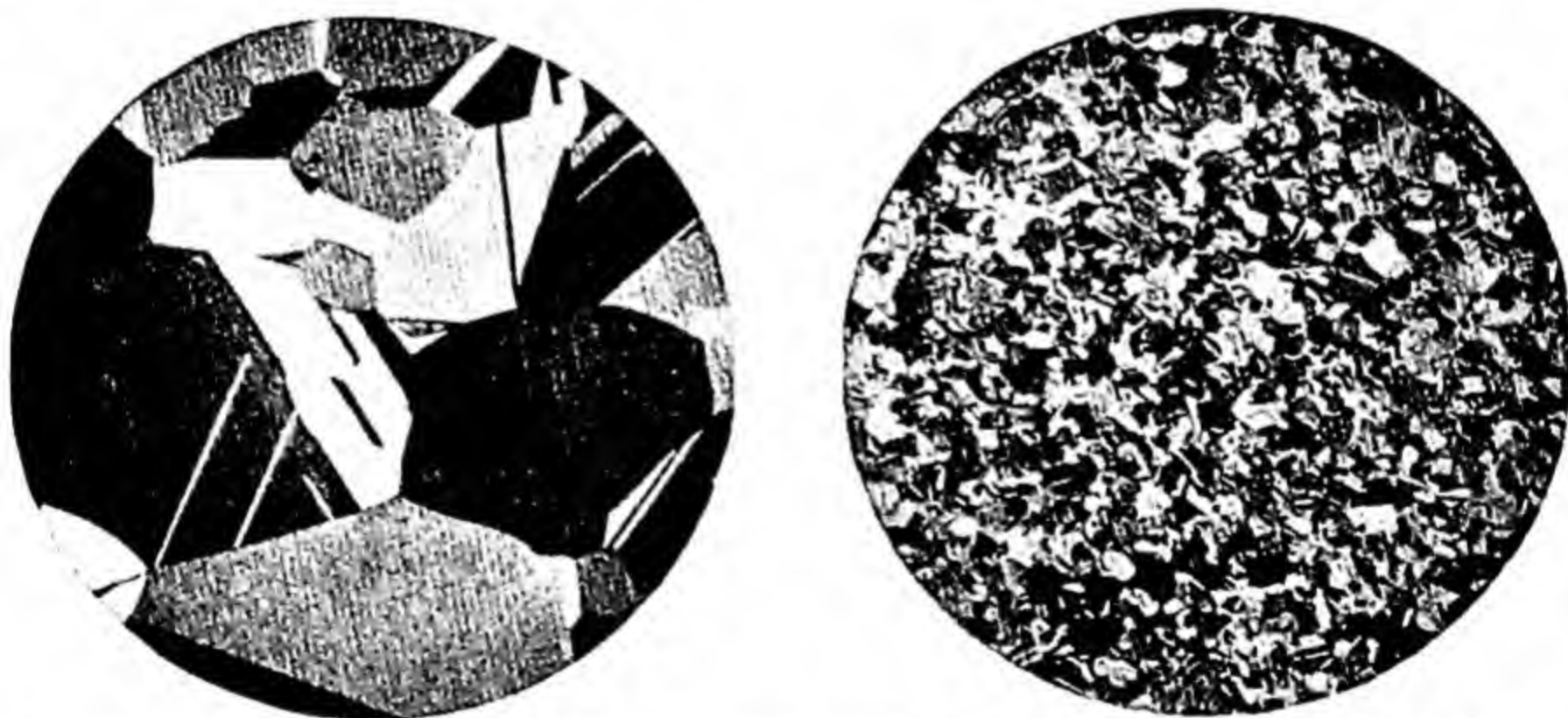


Fig. 145. Beryllium (2%)-copper alloy on the left annealed from 800°C . Coarse structure causing surface roughness in deep-drawn wire. On the right the same alloy to which was added 0.25 nickel. After annealing from 800° the structure becomes much finer. Magnification 75X. (Courtesy American Brass Co.)

SPECIAL ALLOYS

Bearing Metals. The bearing metals which surround revolving shafts are interesting examples of the dispersion of harder solid particles in the softer matrix. These "babbitts," as they are often called, are alloys of tin and antimony, with some copper.

High-speed, high-compression automotive motors make severe demands upon bearing metals. Cadmium-nickel alloys containing from 0.75 to 3.00 per cent nickel have recently come into use in this field.

Today high-speed bearings may be lined with cadmium-silver-copper, cadmium-zinc, or cadmium-nickel, and possibly may be electroplated with indium to increase resistance to oil corrosion.

Corrosion-Resistant Alloys. It is vitally important to find alloys or metals sufficiently corrosion-resistant for use in chemical industry. Monel metal (Cu-Ni) and the 18-8 chrome-nickel stainless steels of low carbon content are much used for this purpose. Some metals resist certain acids and are attacked by others.

Manganese-bronze propeller blades for steamships contain Mn-Cu-Sn-Zn, an alloy resistant to salt-water corrosion.

Stellite, a Co-Cr alloy of great hardness, is so non-corrodible that it is used in surgical instruments.

Low-Melting Alloys. The low-melting alloys, such as Wood's metal or Rose's metal, have an important application. The automatic sprinklers dotting the ceilings of great department stores or factories are merely water pipes closed by a plug of such an alloy. When a fire starts, these plugs melt very soon and release a spray of water. Wood's metal melts at 70° . Solder is another low-melting alloy of value. Each metal in the solid solution lowers the melting point or freezing point of the others, hence the mixture melts at a lower temperature than the constituents. This is the same effect as that produced with water by the addition of salt.

Plumbers' solder (62 per cent lead and 38 per cent tin) is useful because before the eutectic temperature is reached as the solder cools a large mass of lead-rich crystals separates, forming a mushy mass that can be "wiped" on a pipe joint. It begins to solidify at 240° but is not entirely solid until 180° is reached.

High-Melting Alloys. A gas turbine of 10,000 h.p. is feasible — when alloys are prepared to stand the extraordinarily high temperature of operation. At present an alloy steel containing cobalt, chromium and tungsten is used.

Very Hard Alloys. Cast iron (not pure iron) and the bronzes are very hard. Many of the best bronze castings contain 10 per cent tin, 2 per cent zinc, and 88 per cent copper. The tin limit is 33 per cent, forming a very hard, brittle bronze which takes such a high polish that for centuries it was used for mirrors.

Copper is a soft metal and yet its alloy with a very little silver and chromium, "cupaloy," is harder than ordinary steel. Special heat-treatments are necessary in developing this great hardness although copper alone cannot be tempered.

Lead containing several per cent of calcium is too hard to be cut with a hack saw.

High-manganese steels make excellent jaws for rock crushers.

Very Strong Alloys. The alloy steels lead this list with tensile strengths ranging from 40,000 to 500,000 pounds per square inch cross section. Only two per cent beryllium in nickel gives it the tensile strength of steel. Beryllium is to copper what carbon is to iron: a powerful agent in increasing hardness, elasticity, and strength. A new Mg-Li alloy possesses high strength and good ductility.

Vibration-Resistant Alloys. Be-Ni valve springs are almost necessary for the highest-speed airplanes because of the vibration. A steel spring may break after flexing two million times, but a Be-Ni (or Be-Cu) spring will stand flexing twenty billion times. Titanium reduces "fatigue" in steel and is itself highly vibration resistant.

Vanadium steel must be used for auto axles because of the excessive jarring. Common steels may break under difficult road conditions.

Amalgams. An alloy of mercury with other metals, usually powdered, is called an amalgam, as the Ag-Hg used for filling teeth.

By electrolysis of a solution of ammonium chloride in absolute methyl alcohol (not water) McCoy obtained a product at the mercury cathode quite different from ordinary ammonium amalgam. It was a crystalline solid with metallic lustre and the appearance of pure zinc. It remained unchanged for days, at low temperatures. When this solid was added to water solutions of

salts of copper and zinc these metals were precipitated at once. With pure water it forms colloidal mercury and $N(CH_3)OH$. Hence the amalgam probably contained a free complex radical.

COMPOSITION AND USES OF ALLOYS

NAME	PER CENT COMPOSITION	USES
Aluminum bronze	{ Al 7.15 Cu 90.85 Si 2.00	Ornamental
Babbitt	{ Sn 90 Sb 7 Cu 3	Bearings
Brass	{ Cu 73-66 Zn 27-34	Sheets, tubes, cartridges, etc.
Brass, naval	{ Cu 70 Zn 29 Sn 1	Marine condenser tubes
Bronze	{ Cu 88 Sn 8 Zn 2 Pb 2	Strong valves and fittings
Bronze (aluminum)	Cu 90 Al 10	Hard, non-corrodible, ornamental
Chromel	Ni 60 Cr 40	Resistance wire for electric heating (patented)
Dowmetal E.	{ Mg 93.7 Al 6.0 Mn 0.3	As a light, hard alloy
Duralumin	{ Al 94.5 Cu 4.0 Mn 1.0 Mg 0.5	Airplane and auto parts
Fusible (Wood's)	{ Bi 38 Pb 31 Sn 15 Cd 16	Automatic sprinklers, fuse plugs
German Silver	{ Ni 18-25 Zn 20-30 Cu (remainder)	Table ware, cheap jewelry
Magnalium	{ Al 90-94 Mg 10-6	Scientific instruments. Balance beams
Manganese bronze	{ Cu 56 Zn 41 Sn 0.5 Fe 1.0 Mn 0.5 Al 1.0	Propeller blades, non-corrodible and with great wearing qualities
Monel metal	{ Ni 60 Cu 33 Fe. Mn (?)	Almost non-corrodible. Propeller blades, wire, sheets, etc.
Nichrome	{ Ni 75 Fe 12 Cr 11 Mn 2	Electric resistance wire for heaters
Pewter	{ Sn 85-90 Pb 15-10	Platters, bowls, cups, etc. Little used at present

COMPOSITION AND USES OF ALLOYS (*Continued*)

NAME	PER CENT COMPOSITION	USES
Solder (soft)	Pb 62 Sn 38	Plumbers' solder
Solder (low tin)	{ Sn 20 Pb 79 Ag 1	To save tin in emergencies
Solder ("Silma")	{ Ag 85 Mn 15	Solder for welding steel for high temperature operation
Steel (low carbon)	{ C 0.5–0.25 Fe (remainder)	Boiler plate, rivets, sheet, structural work, bridges, shafting
Steel (leaded)	{ 1 part Pb 500 parts steel	Faster machining
Steel (medium carbon)	C 0.4–0.8	General
Steel (high carbon)	C 1.2–1.5	Cutlery, rails, wood-working tools, drills, castings. Saws, files, razors, ball bearings
Steel (stainless 316)	{ Cr 17 Ni 12 No 3 Fe and C	For corrosion-resistance and strength
Stellite	{ Co 80–50 Cr 20–50 W?	Non-corrodible. Used in high-speed tools, cutlery, surgical instruments
Sterling silver	{ Ag 92.5 Cu 7.5	
Type metal	{ Pb 60–85 Sb 8–20 Sn 5–35	Printers' type

STEEL

Cast iron and steel are alloys of Fe with C, Mn, etc., and may well be included here. However, cast iron is placed with the metals (see page 505).

Impurities are usually things to be got rid of, but in the case of iron this idea has to be modified. Pure iron is so soft that it is far surpassed in useful properties by iron containing from 0.1 to 1.0 per cent of carbon, a product known as steel. For example, steel is hard, strong, elastic, and can be permanently magnetized. Of late years, we have gone even so far as to add manganese, chromium, nickel, vanadium, tungsten, and other elements, so that some alloy steels contain four or five elements. But hydrogen is not desired for 0.002 per cent makes steel brittle.

The Bessemer Process. William Kelly, an American, proved in 1852 that the impurities in melted pig iron could be burned out by a blast of air. It was three years later that Bessemer, the Englishman, discovered and patented the same process. This invention enormously increased the world's steel production and thus made possible the great era of railroad building that marked the latter half of the past century. Before 1864 rails were iron. Steel is twice as strong and wears five times longer.

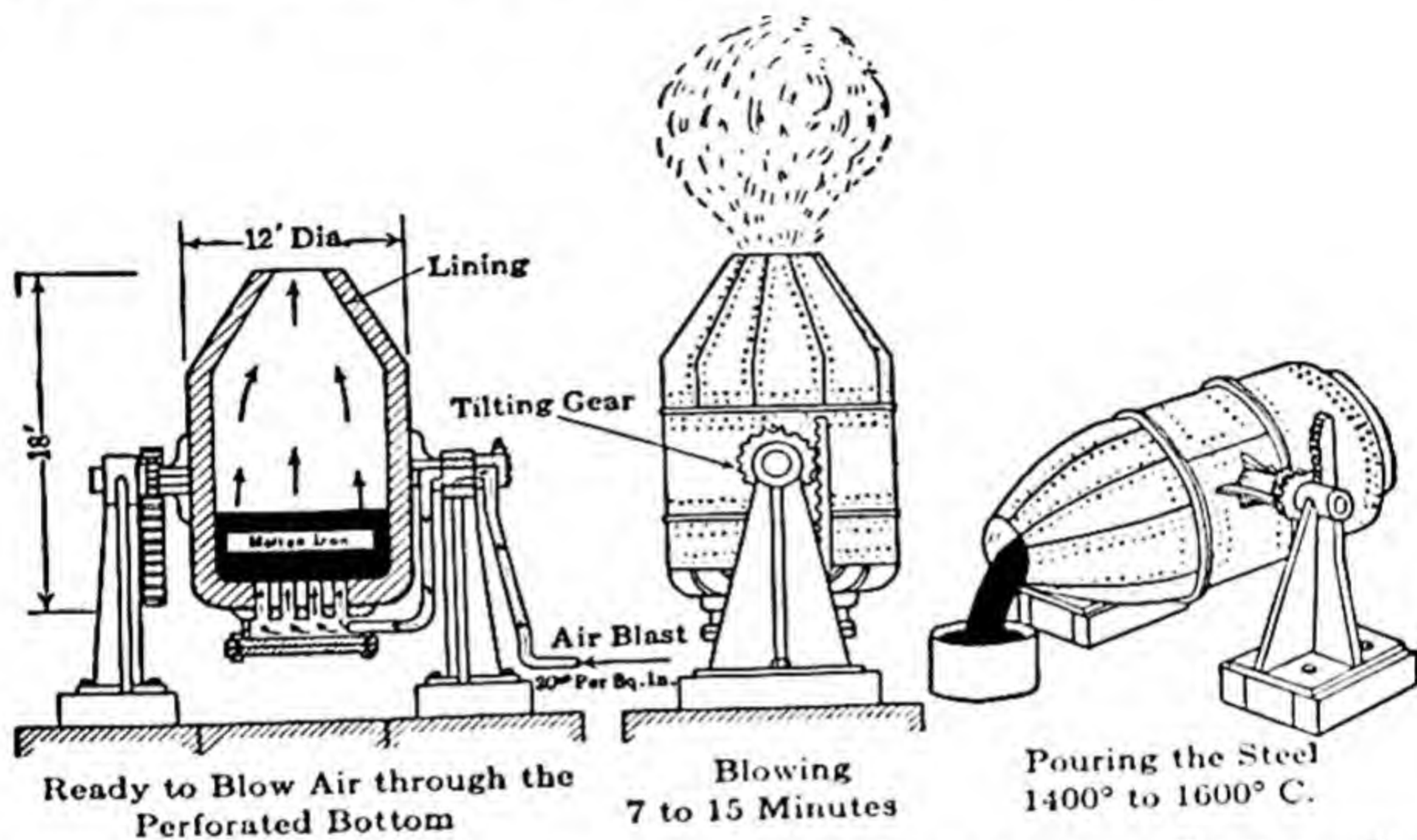


Fig. 146. The Bessemer converter making steel from pig iron. (From a series of lantern slides by J. O. Frank and the Welch Scientific Co.)

The Bessemer converter for iron is a huge steel egg lined with dolomite or siliceous rock, as desired. In a false bottom are many small holes. Below is the wind box into which air is forced through a hollow trunnion. The whole converter can be tilted to any angle. Molten iron is poured in while the converter is nearly horizontal, air is turned on, and the converter raised. Air bubbling up from the small holes at 20 to 30 pounds pressure oxidizes the carbon, silicon, sulfur, phosphorus, and manganese with so much evolution of heat that the iron becomes even more fluid. A dazzling flame and showers of sparks present a magnificent spectacle. After 15 minutes of blowing to oxidize the impurities,

the converter is tilted to pour its contents, 25–50 tons, into a ladle, from which it is poured into a series of ingot molds. At the moment of pouring, the desired amount of carbon (as high-carbon alloys), together with manganese or other elements, is added to the ladle. Since there is much air trapped in pouring, there is danger of weak places in steel rails where such bubbles are found. It is customary to add deoxidizers, which unite with oxygen to form a light slag which floats to the top. Manganese-iron as spiegeleisen has long been used for this purpose, but aluminum shot has become popular with the steel maker, as has silicon or rather ferrosilicon. Sometimes the deoxidizer is added just as the metal is poured. About 12 pounds of manganese per ton deoxidizes and also removes sulfur (as MnS dissolved in the slag). Recently sodium carbonate has been added to aid in sulfur removal.

By a new development in deoxidation of molten steel a metal carrying four per cent carbon is added as the steel is poured from the Bessemer. At the 1600° temperature carbon is a more effective deoxidizer than silicon or manganese.

At each “blow” 25 tons or more of steel are made, so the process is rapid, too rapid for the highest quality. Iron containing much phosphorus must be blown in a converter lined with dolomite or some other basic material. The phosphorus pentoxide formed reacts with this lining to form calcium and magnesium phosphates. In the United States the converters are usually “acid-lined,” that is, faced with siliceous rock, since the ores usually contain very little phosphorus. Open-hearth steel, because of its superior quality, now is produced in greatest tonnage.

The Open-Hearth Process. The open-hearth converter is a furnace with a wide, saucer-shaped hearth and a low roof (Fig. 147), about 40×15 feet; and the charge is 2 feet in depth. The floor lining is a basic mixture of magnesium carbonate, magnetite (Fe_3O_4), and slag. The charge may be 150 tons.

A charge of pig iron and rusty scrap is added with limestone sufficient to flux off the impurities. The fuel is producer gas or an oil spray burning above the charge. The air and gas are both preheated by passing through a checkerwork of fire brick. The

hot gaseous products of combustion pass off through another fire-brick chamber. By frequently reversing the direction of the gases great economy of heating is secured. This is the Siemens regenerative process. About 50 tons of steel, or more, are produced every eight hours. The process somewhat resembles the puddling process in that the oxygen needed is derived from iron

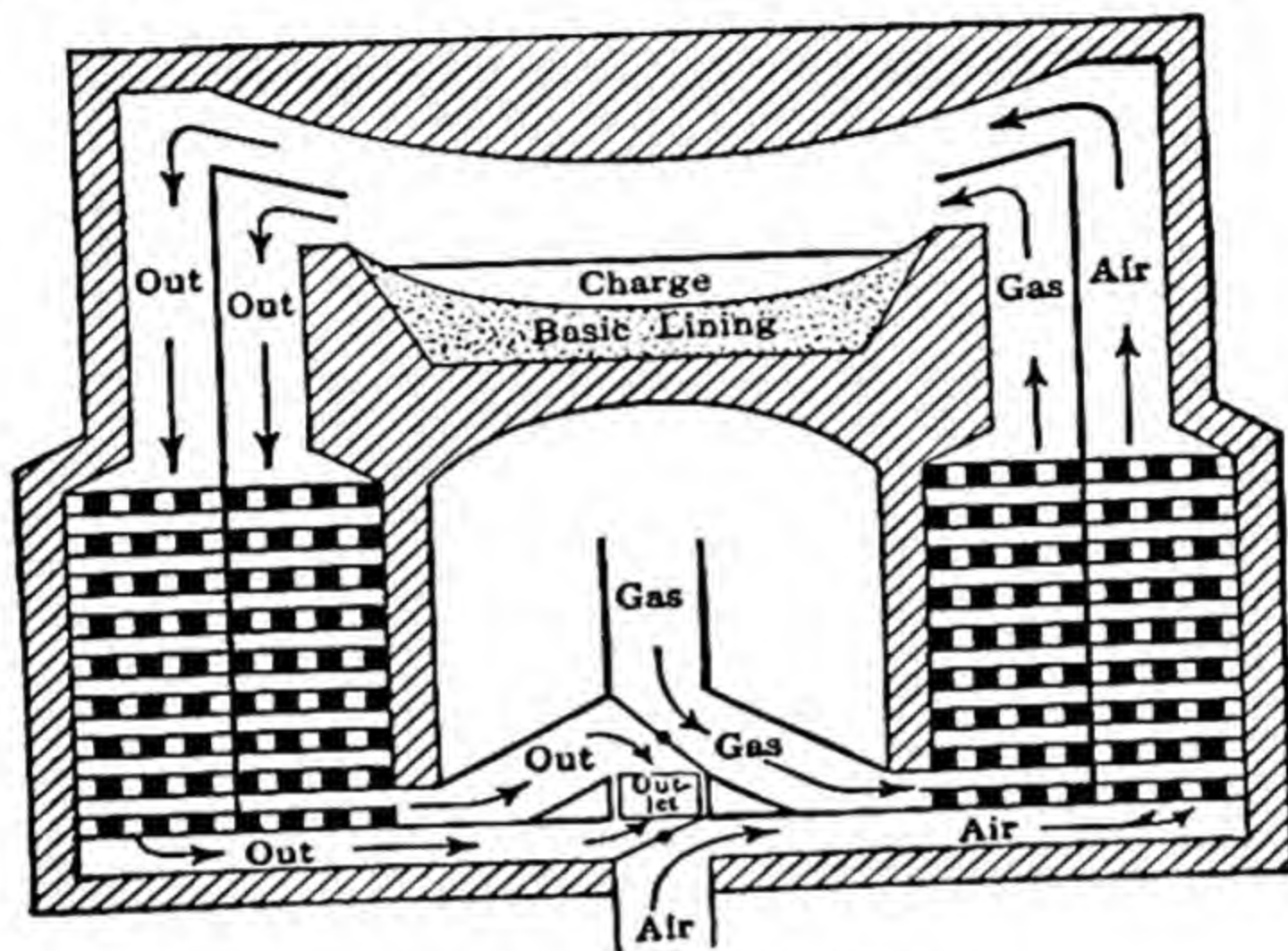


Fig. 147. Open-hearth furnace.

ore and rusty scrap. The necessary carbon, manganese, etc., are added at the moment of pouring. Such steel carries fewer inclusions of FeO and gas than Bessemer steel.

Experiments in 1948 indicated that use of jets of 90 per cent oxygen in the open-hearth may be profitable.

Exercise

1. Which metal is better for fire bars wrought iron or high-carbon steel?

The United States in one prosperous year produced over one-half of the world's pig iron, and of steel nearly 90,000,000 tons.

A large amount of steel is worked over from old "scrap," hence more steel than pig iron is produced. About 91.5 per cent of the total steel in this country is open-hearth, 6.5 per cent Bessemer,

and 2.0 per cent electric furnace. Electric heating in steel processes has certain advantages over coke heating for special products, notably for some of the alloys.

Electric-furnace steel is so free from gas or oxide inclusions and from the worst impurities of all, sulfur and phosphorus, that it is very tough and dependable, and therefore good for auto engines, axles, and wheels.

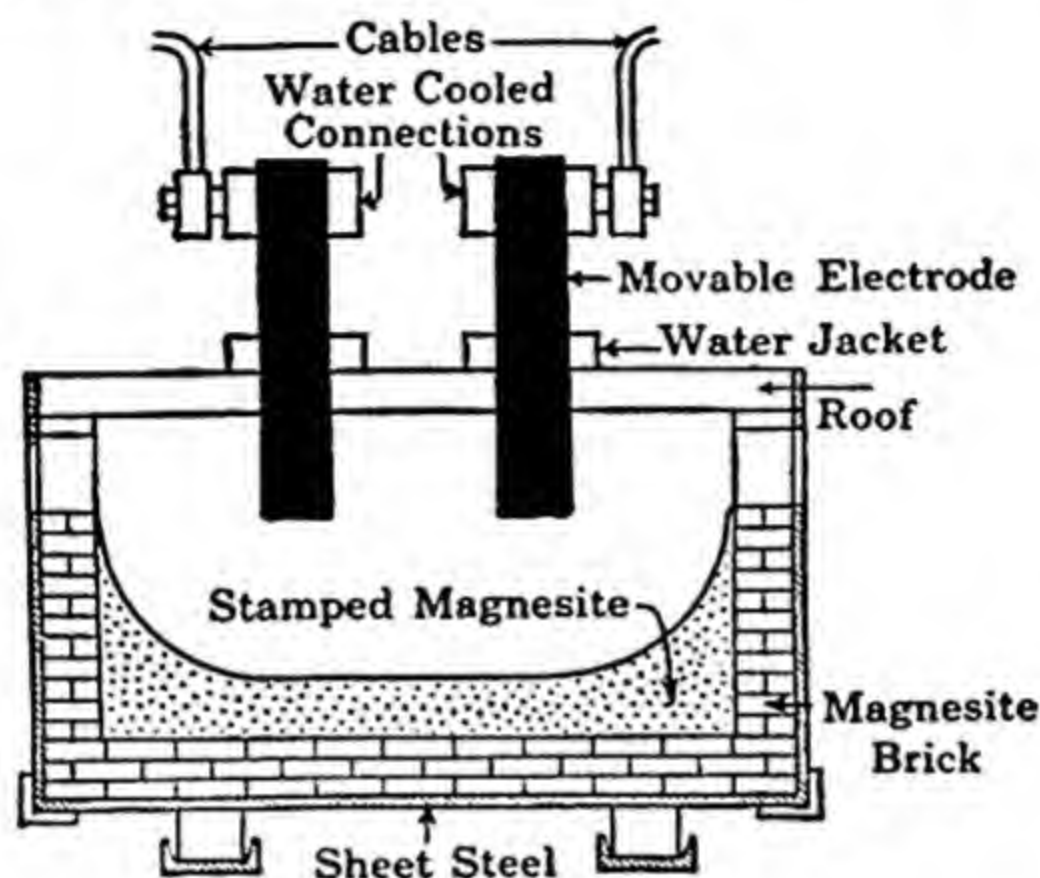


Fig. 148. Electric furnace.

SPECIAL ALLOY STEELS

We could not make autos for less than four times their present cost were it not for the modern development of alloy steels. Crankshafts, driving shafts, transmission shafts, axles, frames, and gears are stronger, tougher, lighter, and stand shocks and strains better because they are made of alloy steel.

Manganese Steel (12 or 14 per cent Mn) if suddenly cooled from the molten state is harder and tougher than any other steel alloy. It is used in the manufacture of grinding machinery, rock crushers, and burglar-proof safes. With a little added molybdenum it is suitable for heavy-duty gears.

Tungsten Steel (such as 18 per cent W, 4 per cent Cr, and 1 per cent V) is self-hardening; that is, a tool of this material hardens on cooling in air without being quenched in oil or water. It also holds its temper when the tool is worked until red-hot from friction. Before the invention of this steel the speed of lathe

work was seriously retarded by loss of temper in the cutting tools. Now the use of tungsten steel has multiplied several times the output capacity of the machine shops of the world.

Molybdenum Steels. Molybdenum (very fortunately produced chiefly in our own country) is replacing part of the tungsten in high-speed tools. To other alloys this element adds toughness, wear resistance, and fatigue resistance.

Molybdenum also forces an even distribution of graphite in gray cast iron.

Vanadium Steel (0.1 to 0.2 per cent V and 1 per cent Cr). When steel is desired to stand the heaviest shocks and vibrations, nothing is quite so effective as a vanadium steel. Axles, cranks, frames, and piston-rods are made of this alloy. Vanadium-steel rods can be twisted and bent double when cold.

In chrome-vanadium steel the chromium content ranges from 2 to 10 per cent. It is used in auto springs, axles, steering gear, etc.

Chrome Steel (2 to 4 per cent Cr). Chromium makes steel extremely hard. Cutting tools of special hardness, and armor plate are made of this alloy.

Nickel Steel (3.5 per cent Ni). This steel resists corrosion, is hard, elastic, and very suitable for armor plate, wire cables, and propeller blades. The auto industry is a leading user.

Nitrided Steel. Hot steel "cracks" ammonia gas and probably forms a nitride of iron on the surface. At any rate the hardest steel surface known is obtained by heating steel 21 hours or more at 625° C. in a stream of ammonia gas. All nitrided steels contain molybdenum, to secure greater depth of nitridation. Hot steel is also surface-hardened by contact with carbon.

Stainless Steel (18 chromium-8 nickel) is, when polished, highly resistant to corrosion. It is much used on the exteriors of office buildings, for certain chemical equipment in industry, and for table knives. The corrosion resistance is increased by the addition of from 1 to 3 per cent molybdenum. These steels cost several times as much as common steel.

Sheet steel for the automobile industry is now made at low cost (and in 80-inch width) in continuous mills half a mile long. Such a mill costs \$20,000,000 or more.

The Heat-Treatment of Steel. The two most important modifications of iron are *alpha-iron* (like the pure iron of wrought iron), which is soft, ductile, and magnetic, (stable below 900°); and *gamma-iron*, stable above 900° C. The latter is denser and only slightly magnetic.

The alpha-iron crystal lattice is the body-centered cube type with iron atoms at every corner and one in the center, while

gamma-iron has a face-centered cubic lattice with iron atoms at the corners and at the center of each face. Alpha-iron is often called *ferrite*.

Sudden cooling of white-hot steel gives a supersaturated solution of carbon as Fe_3C in alpha-iron (*martensite*), hard and brittle. Slow cooling gives time for thin plates of *cementite*, Fe_3C , to form, alternating with alpha-iron masses, the two together forming *pearlite*. Because of the large amount of alpha-iron this steel is soft and ductile.

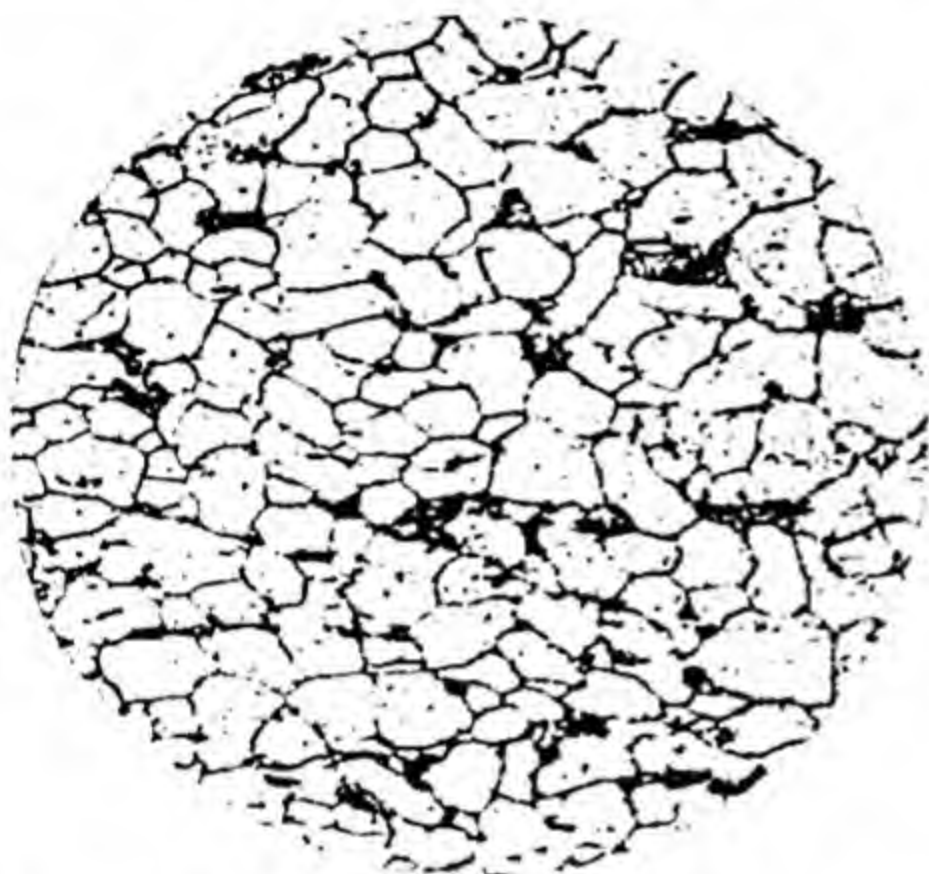


Fig. 149. Photomicrograph of a cold-drawn steel wire, 0.1 per cent carbon. Magnification, 250. The white areas of pure iron (ferrite) are surrounded by dark areas of pearlite containing the iron carbide, Fe_3C , and iron. (Courtesy H. B. Pulsifer.)

Manganese and nickel help to keep the carbon in solid solution (*austenite*).

Annealing, by reheating a quenched steel to 200° – 350° C., allows some crystal growth, some separation of hard cementite, Fe_3C , and some release from strains. Any intermediate degree of hardness may be secured by tempering.

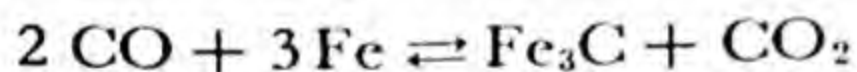
Austenite is a solid solution of Fe_3C in gamma iron but on slow cooling it changes into Fe_3C and ferrite. The original austenitic condition is partly preserved by sudden cooling, resulting in a very hard product.

If steel is rolled above 900° C. (austenite state, dissolving up to 1.7 per cent carbon as solid solution), it changes on cooling below this temperature into the

alpha state (dissolving only up to 0.04 per cent carbon) and setting up enormous internal stresses because the alpha form shows a volume expansion of 1 per cent. Annealing to relieve these stresses is necessary.

In case-hardening, a low-carbon steel is held for several hours in charcoal and bone ash or a reducing gas or sodium cyanide at 1000°C .; carbon is taken up by the surface, yielding a steel that is hard on the surface and tough in the interior. Gears must be case-hardened. Steel is hardened by 0.02 per cent boron as much as by 250 times that much nickel.

Reduction of CO_2 by hot carbon yields CO , which penetrates slightly into the metal where it reacts to form hard cementite, Fe_3C :



Localized hardening of certain wearing surfaces may be obtained by quick induction heating with immediate chilling.

Exercises

2. If we had no alloys and had to depend upon practically pure metals, what difference would it make in our daily life?

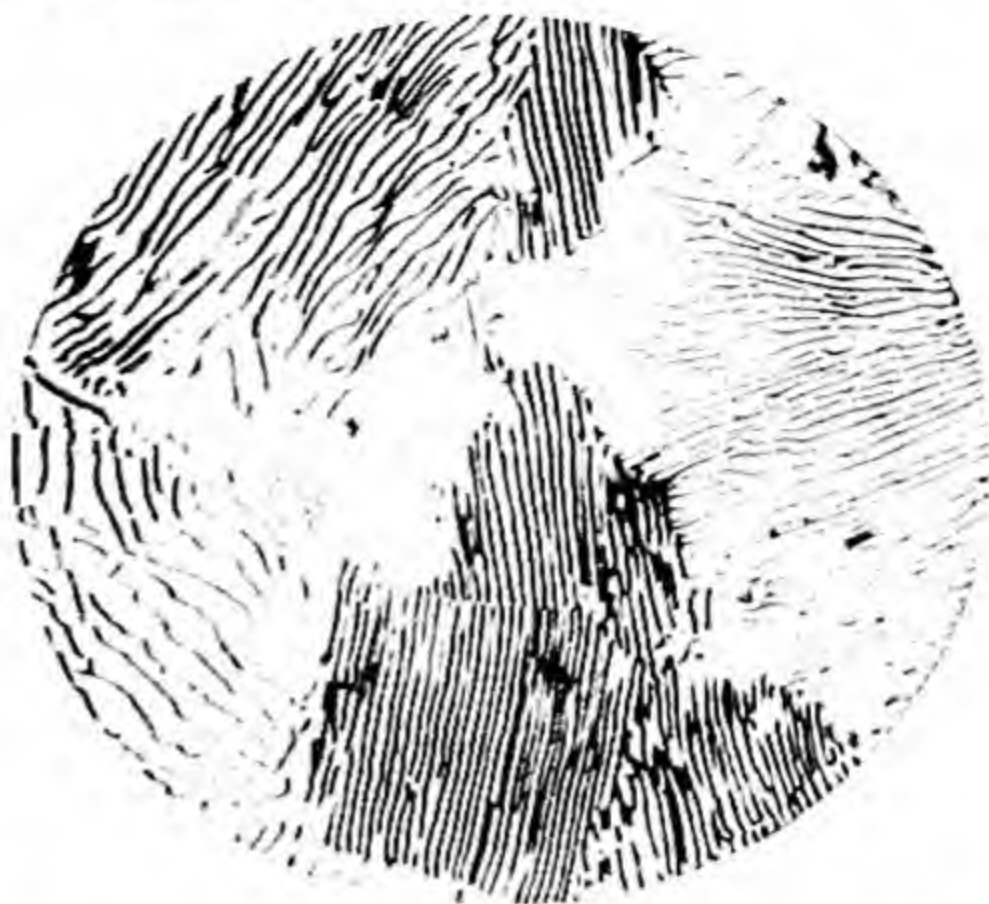


Fig. 150. The effect of heat-treatment of steel. A coarse structure is obtained by cooling this 0.89 per cent carbon steel from 877°C . at the rate of 3°C . per minute.



Fig. 151. The same steel as in Fig. 150. The finer structure is obtained by sudden water cooling from 877°C . and then tempering one hour at 550°C . Magnification of polished and etched surface, 2000. (Courtesy J. R. Vilella, United States Steel Corporation.)

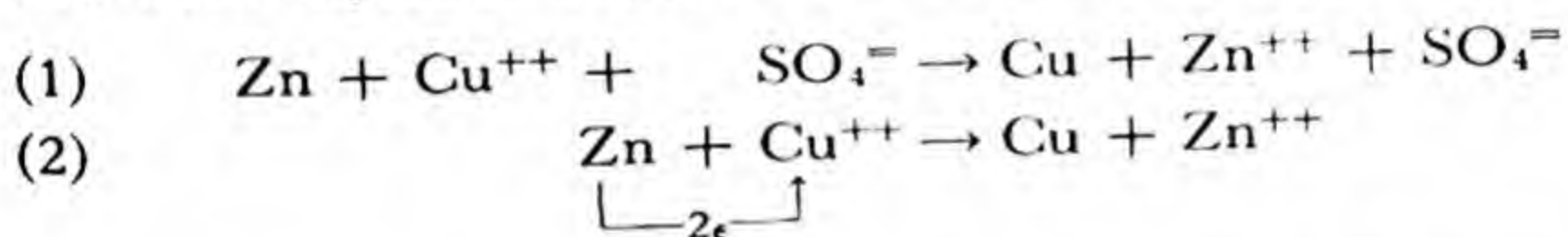
3. Aluminum melts at 660° and antimony at 630° but a certain alloy of the two metals melts at 1066° . How can this be?
4. What substitutes could we use for copper alloys if supplies of copper were exhausted?
5. Could you describe an ideal alloy?
6. In what alloy is chromium valuable? What is the chief chromium ore? Where mined?
7. What weight of charcoal must be added to 6 tons of pure, melted iron to make a steel containing 2 per cent carbon?
8. What are some of the bearing alloys?
9. Explain the heat treatment of steel.

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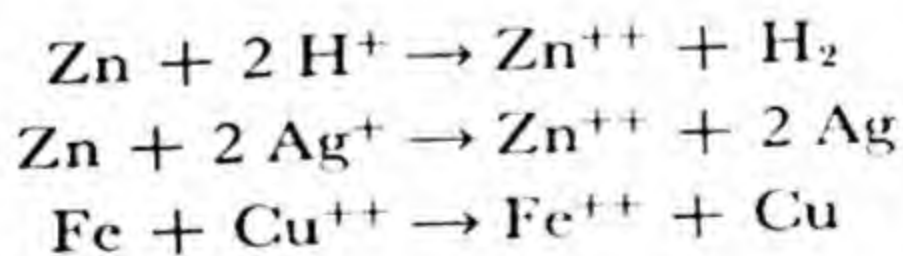
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Chapter 50 ELECTROCHEMISTRY

Ionic Displacement. Zinc dust, shaken with a solution of copper sulfate, removes the blue color with evolution of heat. After filtering, metallic copper is found on the filter and a solution of zinc sulfate in the filtrate. In other words, blue copper ions have become red copper molecules; and zinc molecules have become zinc ions. Equation (2) gives the essentials of equation (1):



In reality the zinc atom in gaining two positive charges has given away two electrons (negative charges of electricity) to the blue copper ion. Loss of electrons by a metallic atom means the formation of a positive ion. The displacement of hydrogen from acids is similar:



Evidently a displacement series of the metals can be arranged in which a given metal will displace from salt solutions any metal below it, but will in turn be displaced by any metal above it. Such a series has a number of names. It was given on page 99 as the "activity series" with the most active metals at the top. Now we see that those at the top have the greatest tendency to lose electrons — to go into solution as ions. Hence the name, "solution

tension series" or "electrochemical series." An abbreviated list of the metals in proper order appears below.

Electric Cells. During the addition of zinc dust to a copper sulfate solution chemical energy is transformed into heat. But

MOST ACTIVE

Li
K
Na
Ba
Sr
Ca
Mg
Al
Mn
Zn
Cr
Fe
Co
Ni
Sn
Pb
H
Cu
Sb
Hg
Ag
Pt
Au

LEAST ACTIVE

it is possible to transform chemical energy into electricity by placing two metals (separated) in a solution of acid, base, or salt and connecting the metals outside by a wire. Solutions of zinc sulfate and copper sulfate may be kept apart by a porous clay wall which permits ions to wander through when attracted but hinders ordinary diffusion (Fig. 152). A zinc plate is placed in the zinc sulfate compartment and a copper plate in the copper sulfate compartment. On connecting the two plates by a wire a current of electrons flows along the wire from zinc to copper and through the solutions to the zinc. This device is a primary cell (as differing from a secondary or storage cell) and converts chemical energy into electrical energy. The zinc, with a greater solution tension, or pressure, than the copper, throws atoms into solution as ions. This means that some zinc atoms give up electrons to the rest of the zinc plate. These electrons flow along the wire (current of negative electricity) to the copper plate, where they are readily taken up by the adjoining copper ions. This action neutralizes the charge on the copper ions and causes a deposition of metallic copper on the plate. Finally the zinc plate is dissolved or all the copper ions are removed. The excess Zn^{++} ions attract SO_4^- from the other compartment, so all portions of the solutions are kept electrically neutral. In all cases the more active metal dissolves. The direction of the current, as arbitrarily named, is opposite to the flow of electrons along the wire. This decision as to the direction of flow was made before scientists knew anything about electrons.

The Gravity Cell is a convenient arrangement of the zinc-

copper cell. The copper plate lies in a saturated solution of copper sulfate, while the zinc plate (shaped like a crowfoot) is hung over the edge of the jar in the lighter solution of zinc sulfate or dilute sulfuric acid. Thus gravity helps to keep the two solutions apart without a diaphragm. This battery, in either form, is often called the Daniell cell.

The *Lalande Cell* (zinc and copper oxide plates in sodium hydroxide solution) operates at 0.6 to 0.7 volt and can deliver

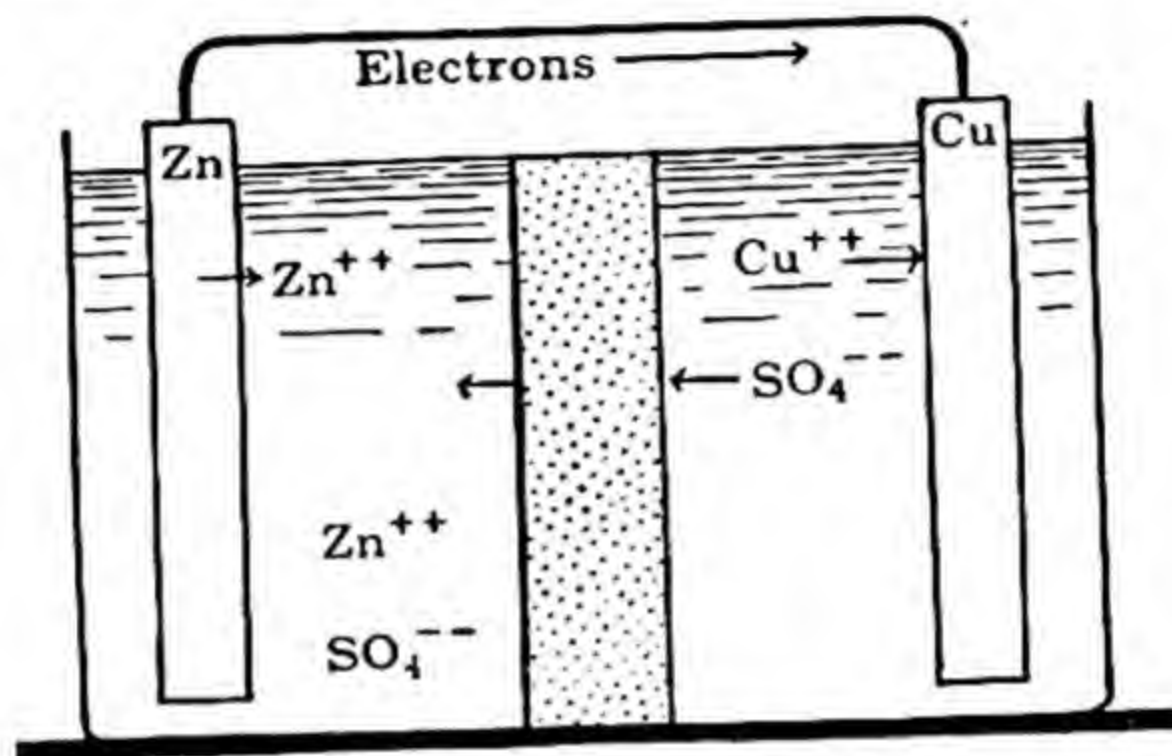
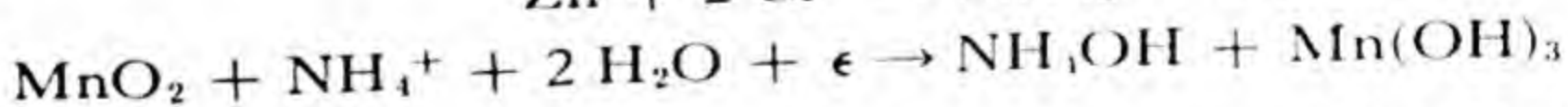


Fig. 152. A primary cell.

heavy current. A million such cells are in use for railway signal operation.

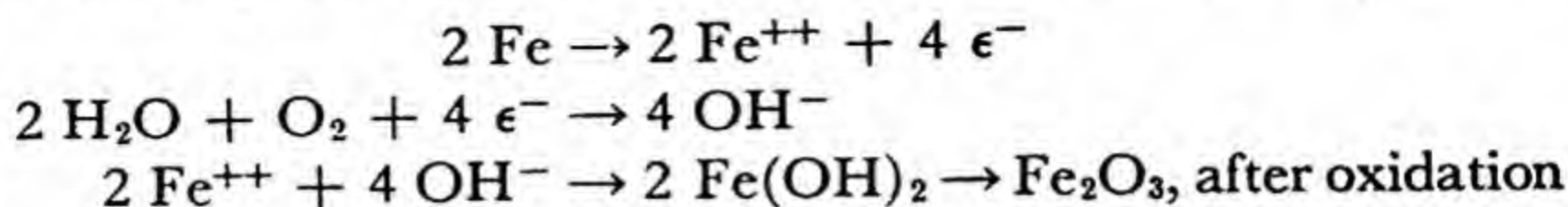
The *Dry Cell*, so familiar in flashlight use, consists of a carbon rod in a zinc can filled with a solid but moist paste of carbon, manganese dioxide, zinc chloride, and ammonium chloride. The carbon and zinc are the poles, while the manganese dioxide acts as a depolarizer, preventing formation of a film of hydrogen on the carbon.



Over 600,000,000 of these dry cells are in use in the United States.

A good flashlight cell may have an energy output sufficient to raise its own weight (90 g.) to a height of 15 miles.

Electrolytic Corrosion. By the electrolytic theory of steel corrosion the impurities act as anodes and the iron as cathode.



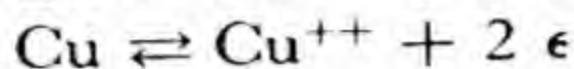
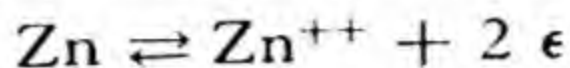
It has been shown that a small electric current imposed on this system can counteract the above effects. Furthermore a very active metal such as magnesium, connected with the steel or iron, will form a galvanic battery in moist soil thus protecting the iron while magnesium dissolves. We could profitably use 60,000,000 pounds of magnesium a year in protecting soil piping.

Electromotive Force. The force that drives the electrons along a metallic circuit is termed *electromotive force* (E. M. F.) or voltage, and its unit of measurement is the volt. The difference in this pressure or potential between the two poles of a Daniell cell is 1.10 volts. Other cells, such as the Clark and Weston, are better standard cells. If a cell is made of two metals close together in the electromotive series, the voltage is very low. The farther apart they are in the series the higher the voltage.

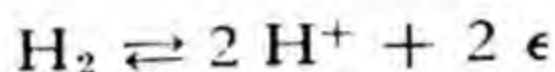
Electric eels may shock with a potential of 200 volts.

Normal Potentials. Any metal in water or water solution has a tendency to throw atoms into solution as ions. There is an actual solution tension differing in degree with the position of the metal in the activity series. In the case of zinc immersed in a solution of zinc salt (that is, in a solution already containing Zn^{++} ions) the tendency of the neutral zinc atoms on the surface of the plate to give up electrons to the rest of the plate is opposed by the tendency of Zn^{++} ions to take up electrons from the plate. With such an active metal as zinc the former tendency is the greater and the metal plate soon becomes negative from the electron donations while the solution with a certain excess of Zn^{++} ions becomes positive with respect to the plate. A difference of electric potential is set up. Of course, the greater the concentration of the Zn^{++} ions in solution, the greater the tendency of Zn^{++} to take electrons from the plate and the negative potential of the plate is lessened.

With the less active metals like copper in a solution of a copper salt the concentration is generally sufficient to make the tendency of Cu^{++} ions to take on electrons from the atoms of the plate greater than the opposing tendency and the copper plate actually becomes positive with respect to the solution:



Even a film of hydrogen gas in contact with a conducting electrode like platinum has a tendency to ionize, to donate electrons to the obliging platinum electrode, making it negative. However, in a solution of H^+ ions, an acid solution, this tendency is opposed by that of the H^+ ions already there to take on electrons from this same platinum plate:



The Hydrogen Electrode. The hydrogen electrode is merely a sheet of platinum with a roughened surface of platinum black saturated with hydrogen gas by a steady stream of the gas at one atmosphere pressure, immersed in a solution containing hydrogen ions and in contact with an atmosphere of

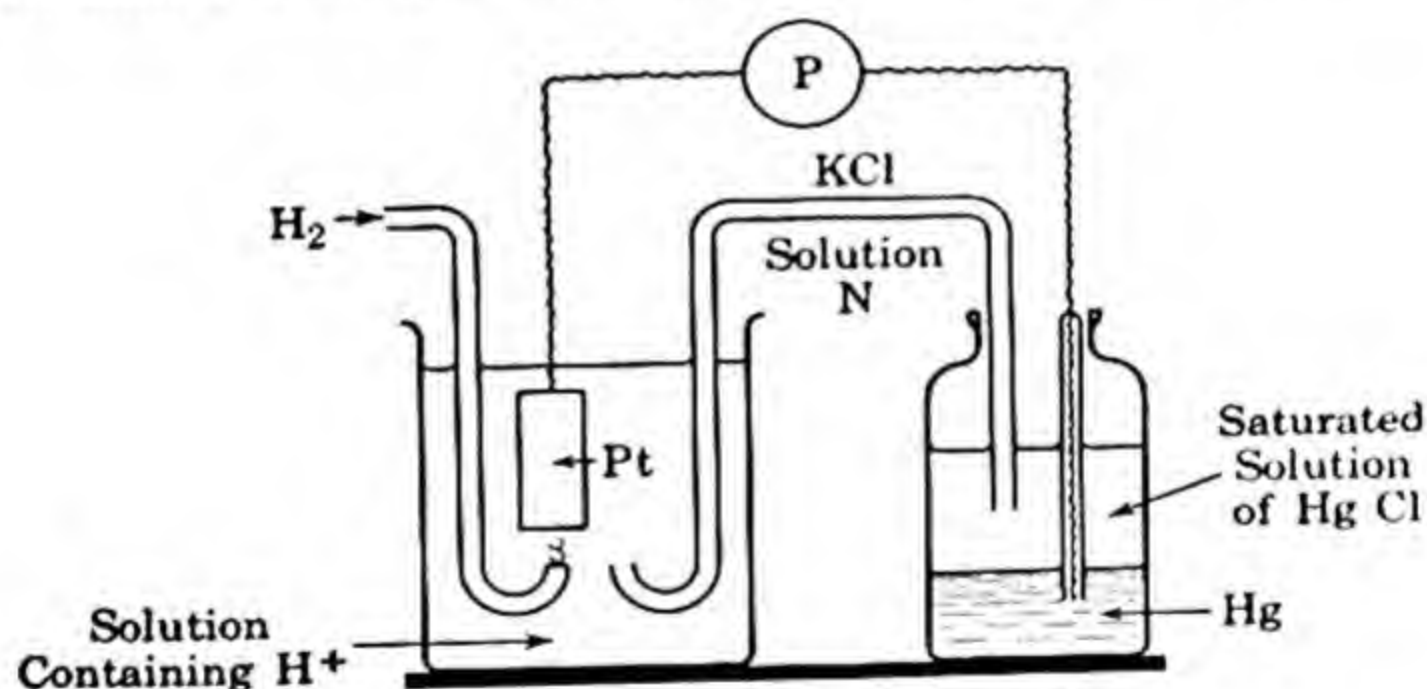


Fig. 153. The hydrogen electrode.

hydrogen gas. Of course, the voltage or potential varies with the concentration of the H^+ ions. With an acid solution of known concentration this half cell becomes a standard cell, with known potential. Joined to a standard calomel electrode for the other half cell, it furnishes a combination whose net potential is the algebraic difference between the two electrode potentials.

Using the unknown solutions as the liquid to surround another platinum black electrode also joined to a second standard calomel electrode, the potential developed by this cell may be compared with that developed in the other.

The H^+ ion concentration of the unknown acid solution is then readily calculated and usually stated as the pH value (Appendix).

Purely for convenience the potential of hydrogen against a N solution of its own ions is taken as zero. In the table below, the metals with a greater tendency than hydrogen to give up electrons to the neutral metal plate are marked with a negative sign because the neutral plate thus becomes negatively charged with electrons donated.

POTENTIALS OF METALS IN CONTACT WITH N SOLUTIONS OF THEIR OWN IONS

(Electromotive Series)

K	-2.92	Fe (Fe ⁺⁺)	-0.44	Cu (Cu ⁺⁺)	+0.34
Ca	-2.76	Sn (Sn ⁺⁺)	-0.14	Hg (Hg ⁺)	+0.80
Na	-2.71	Pb (Pb ⁺⁺)	-0.13	Ag	+0.80
Mg	-1.55	H ₂	0.00	Au (Au ⁺)	+1.5(?)
Al	-1.34				
Zn	-0.76				

Typical reaction, $K - e \rightleftharpoons K^+$

It is, of course, easier to discharge metallic ions on platinum than on more active metal cathodes in electrolysis because the solution tension of the platinum itself is so small. Yet when the platinum becomes covered with a layer of hydrogen gas as sometimes happens, the discharge is no longer against a platinum plate but against a hydrogen plate.

From a table of potentials the voltage of any combination may be calculated. It is merely the difference in potential between the two elements. For example, the voltage of the Daniell cell (Cu - Zn) is $+0.34 - (-0.76) = 1.10$ volts.

Decomposition Potentials. The decomposition potential of a substance in solution is the potential difference just sufficient to cause continuous electrolysis. Naturally it is affected by concentration, temperature, and polarization of the poles. A few values are quoted from Koehler for normal solutions with platinum electrodes.

CuSO ₄	0.80 volts	CaCl ₂	3.05 volts (650°)
AgNO ₃	0.70	KOH	2.4 (200°)
H ₂ SO ₄	1.67	NaOH	2.38 (180°)
HNO ₃	1.69	NaCl	2.65 (800°)
NiSO ₄	2.09		(Dry fused)
NiCl ₂	1.85		
(In aq. sol.)			

In a solution containing two salts with widely different decomposition potentials it is possible to use a current such that

only one metal will be plated out. (Which one?) With certain pairs of metals the addition of potassium cyanide to their salts will bring their decomposition potentials so near together that these metals are deposited together as an alloy.

The decomposition voltage of an electrolyte varies with the nature of the electrodes. Any excess voltage over the algebraic sum of the reversible electrode potentials required for discharge of ions is called overvoltage. The overvoltage for discharge of hydrogen ion on rough platinum is slight, on smooth platinum several times as large, and on mercury four times as much as on smooth platinum.

Electric Energy. Electric energy is measured by the product of the intensity factor times the quantity factor. The volt is the unit of intensity and the coulomb the unit of quantity. Since the flow of water in a pipe leading from an elevated reservoir is somewhat comparable to the flow of electricity, we may consider the difference in electric potential between any two points in a circuit as analogous to the difference in "head" or pressure of water at the reservoir and at the open tap. The unit of actual quantity of water is the gallon, no matter what the pressure or rate of flow. The coulomb is likewise a unit of actual quantity of electricity. A gallon of water delivered under a definite pressure delivers a definite amount of energy to a water motor. So a coulomb of electricity delivered under a certain voltage or electrical pressure delivers a definite number of joules of energy:

$$\begin{aligned}1 \text{ volt} \times 1 \text{ coulomb} &= 1 \text{ joule} \\1 \text{ joule} &= 0.239 \text{ cal.}\end{aligned}$$

A simple definition of the coulomb may be taken from the fact that 96,500 coulombs of electricity (the faraday) will discharge one gram-equivalent weight of any ion during electrolysis. When one gram-equivalent weight of zinc displaces copper from a solution of a copper salt, 25,050 cal. of heat are liberated.

Exercise

1. Calculate how many coulombs are delivered in a Daniell cell when one gram-equivalent weight of zinc is dissolved. Give the heat equivalent of the electrical energy evolved.

The *rate* of delivery of a given number of joules is important. One coulomb per second means a current strength of one *ampere* (similar to one gallon of water per second). The unit of rate of delivery is the *watt*:

$$1 \text{ ampere} \times 1 \text{ volt} = 1 \text{ joule per sec.} = 1 \text{ watt}$$

The horsepower is 746 watts (about as much energy as a common electric iron uses). A 40-watt lamp on a 110-volt circuit must use a 0.36 ampere current:

$$\begin{aligned} x \text{ amperes} \times 110 \text{ volts} &= 40 \text{ watts,} \\ x &= 0.36 \text{ ampere} \end{aligned}$$

Amperes measure the number of electrons passing a given point within a given time. Voltage measures their pressure. With a current of 1 ampere 6.281 billion billion electrons pass a given point in 1 second.

Electric energy is sold by the kilowatt (1000 watts) hour. To convert kilowatt hours into horsepower hours:

$$\text{kw hours} \times 1.341 = \text{horsepower hours}$$

Electricity in favored localities may sell below one cent per kilowatt hour if used for power (in great quantities) but the average consumer is not favored with such a price. In this country he pays about 5 cents.

The Lead Storage Battery. A charged lead storage cell consists of a lead plate surfaced with lead dioxide as the positive pole and a second lead plate surfaced with spongy lead as the negative pole — both immersed in 20 per cent sulfuric acid.

When the two poles are connected by a metallic circuit some of the lead atoms on the surface of the lead plate give up electrons to the rest of the plate (making the plate negative) and go into solution as Pb^{++} ions. They do not go far, however, for they meet $\text{SO}_4^{=}$ ions in the solution and are re-deposited on the plate as insoluble PbSO_4 .

The two electrons given to the lead plate, when Pb^{++} ions are formed, travel along the metallic conductor to the brown lead dioxide plate, PbO_2 . There they unite with H^+ ions of the solu-

tion which on discharge promptly reduce the PbO_2 to PbO , a basic oxide that readily reacts with sulfuric acid to form PbSO_4 .

Discharge

- (1) $\text{PbO}_2 + 2 \text{H}^+ + 2 \epsilon \rightarrow \text{PbO} + \text{H}_2\text{O}$
- (2) $\text{PbO} + \text{H}_2\text{SO}_4 \rightarrow \text{PbSO}_4 + \text{H}_2\text{O}$
- (3) $\text{Pb} + \text{SO}_4^{=}\text{ } \rightarrow \text{PbSO}_4 + 2 \epsilon$

On passing a current through the exhausted cell (as in electroplating) sulfuric acid is electrolyzed, its H^+ ions discharged on the PbSO_4 surface of the lead electrode reducing the lead sulfate

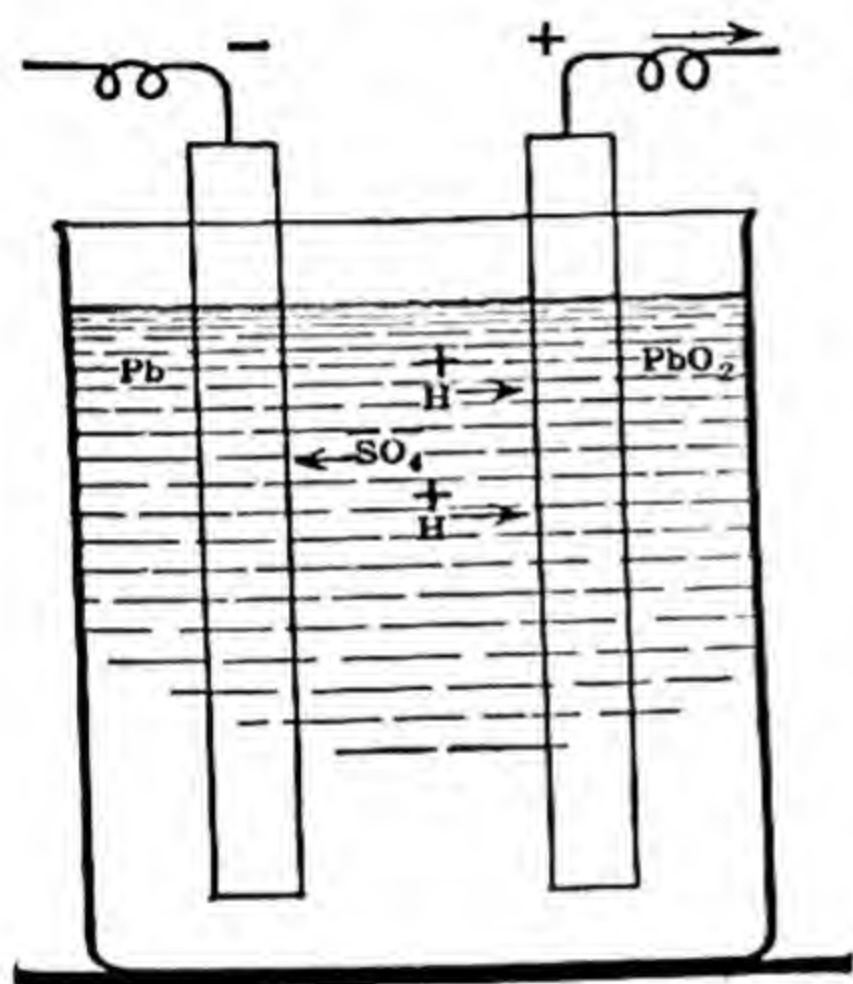


Fig. 154. A charged cell.

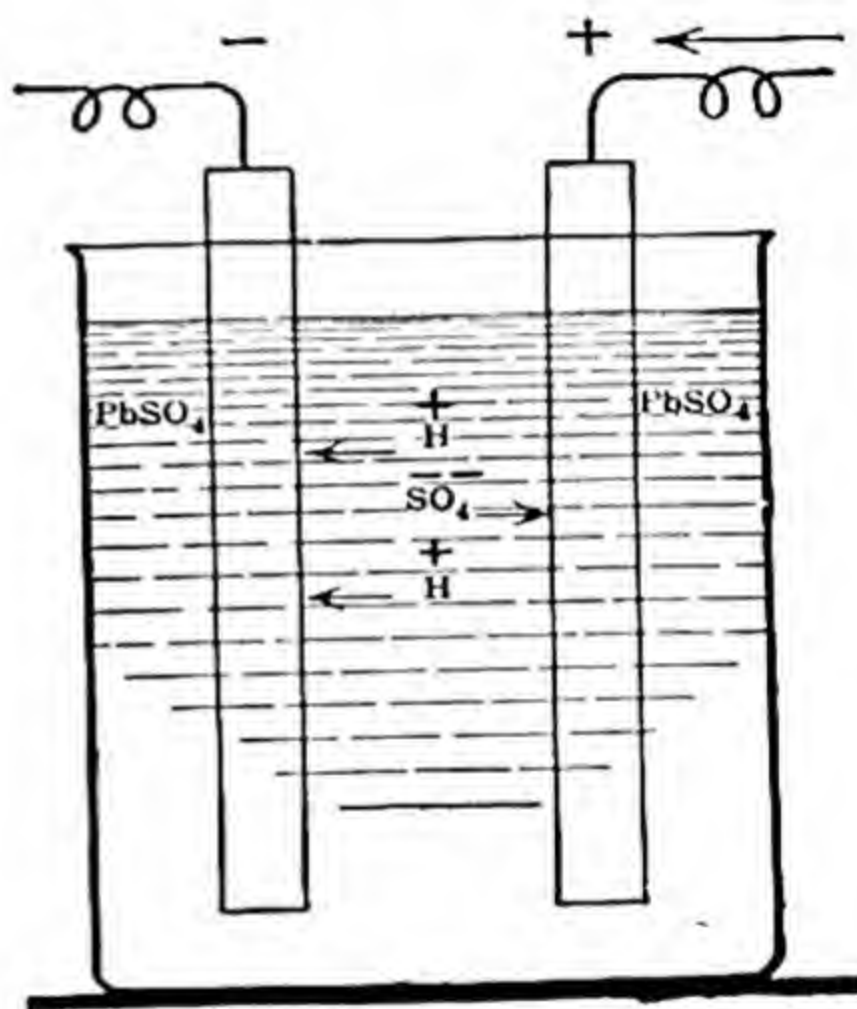


Fig. 155. A discharged cell.

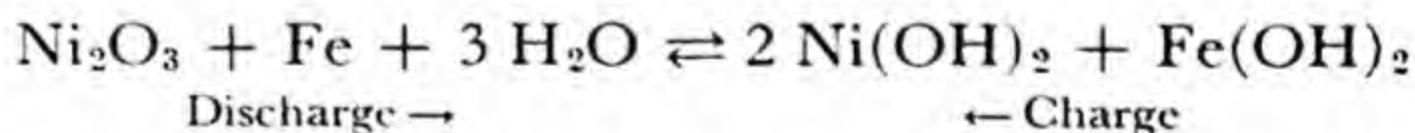
again to the original spongy lead and forming more H_2SO_4 . At the other electrode (brown PbO_2 now surfaced with PbSO_4) the current discharges $\text{SO}_4^{=}$ ions which then unite with the PbSO_4 to form $\text{Pb}(\text{SO}_4)_2$, lead disulfate. This, however, is easily hydrolyzed to the original brown PbO_2 , lead dioxide, and to H_2SO_4 .

Charge

- (4) $\text{PbSO}_4 + 2 \text{H}^+ + 2 \epsilon \rightarrow \text{Pb} + \text{H}_2\text{SO}_4$
- (5) $\text{PbSO}_4 + \text{SO}_4^{=}\text{ } \rightarrow \text{Pb}(\text{SO}_4)_2 + 2 \epsilon$
- (6) $\text{Pb}(\text{SO}_4)_2 + 2 \text{H}_2\text{O} \rightarrow \text{PbO}_2 + 2 \text{H}_2\text{SO}_4$

The action in charging is just the opposite of that in discharging. It is chemical energy that is stored up, not electrical. There is plenty of precedent for the formation of lead disulfate at the anode during charge. Persulfates are actually prepared by anodic oxidation. Furthermore, Evans (*Metals and Metallic Compounds*, Vol. IV, p. 254, 1923) describes the preparation of $\text{Pb}(\text{Ac})_4$ and its hydrolysis to PbO_2 , as well as $2 \text{NH}_4\text{Cl} \cdot \text{PbCl}_4$ and its similar hydrolysis. In practice it is unwise to convert too thick a layer of the plates into lead sulfate, for regeneration becomes difficult, possibly due to a lack of permeability. Nor should a discharged cell stand long before charging. Otherwise the lead sulfate coating becomes more compact. The normal voltage of such a cell, fully charged, is about two volts, but this falls on discharge. Thus there are two ways of learning the condition of the cell: measuring the density of the acid, or the potential fall between the poles. Since sulfuric acid is used up on discharge (the density of the liquid falling to 1.10), and since sulfuric acid is re-formed on charge (with a rise in density to 1.30) it is a simple matter to learn the cell condition.

Storage cells are used in submarines, in small isolated lighting plants, for self-starters in autos, and for many other purposes where direct current is needed. It is interesting to compare the Edison cell with the lead cell. In the Edison type a 21 per cent solution of KOH is the electrolyte, and the poles are iron and an oxide of nickel:



Exercises

2. What is the source of the current in a Daniell cell?
3. A certain electric iron uses 1000 watts for three hours. How much will the current cost at 5 cents per kilowatt hour if the iron is used continuously for three hours?
4. How much silver will be deposited by a current of 5 amperes in 50 minutes?
5. If zinc costs \$0.15 per kilogram, what would it cost per kilowatt hour to draw current from a Daniell cell, ignoring the cost of the copper sulfate? How does this compare with the rate in your town?

6. How much electrical energy is obtained when 600 g. of zinc dissolve in a Daniell cell?
7. What will be the voltage of the following cells: Zn-Pb; Pb-Ag; Cu-Au; Sn-Hg; Ni-Hg?
8. What current strength will be required to deposit 80 grams of lead in 45 hours?
9. When 415 ampere hours of current are taken from a lead storage cell on discharge what weight of sulfuric acid disappears from solution and what weight of water is formed?
10. How many coulombs of electricity flow through an electrolytic cell in plating out 90 grams of cadmium on a cathode?
11. If a current of 200 amperes flows through a solution of copper sulfate for 55 minutes how many grams of copper will be plated out?
12. If you tried to invent a better storage cell, what plates and solution would you have in mind?

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Chapter 51 THE ALIPHATIC HYDROCARBONS¹

Organic Chemistry or the chemistry of carbon compounds deals with 400,000 or more compounds while inorganic chemistry deals with only 90,000.

Homologous Series. There are several hundred hydrocarbons known (compounds of hydrogen and carbon), most of them being found in petroleum, natural gas, asphalt, and coal-tar products. These are divided into several series, with some very definite relationships between the members.

METHANE SERIES C_nH_{2n+2}		ETHYLENE SERIES C_nH_{2n}		ACETYLENE SERIES C_nH_{2n-2}		BENZENE SERIES C_nH_{2n-6}	
Methane	CH ₄			{ (Ethine or) Acetylene			
Ethane	C ₂ H ₆	Ethylene	C ₂ H ₄		C ₂ H ₂		
Propane	C ₃ H ₈	Propylene	C ₃ H ₆	Propine	C ₃ H ₄		
Butane	C ₄ H ₁₀	Butylene	C ₄ H ₈	Butine	C ₄ H ₆		
Pentane	C ₅ H ₁₂	Pentylene	C ₅ H ₁₀	Pentine	C ₅ H ₈		
Hexane	C ₆ H ₁₄	Hexylene	C ₆ H ₁₂	Hexine	C ₆ H ₁₀	C ₆ H ₆	Benzene
Heptane	C ₇ H ₁₆	Heptylene	C ₇ H ₁₄	Heptine	C ₇ H ₁₂	C ₇ H ₈	Toluene
Octane, etc.	C ₈ H ₁₈	Octylene	C ₈ H ₁₆	Octine	C ₈ H ₁₄	C ₈ H ₁₀	Xylene

(Ethylene is often called ethene but not ethine.)

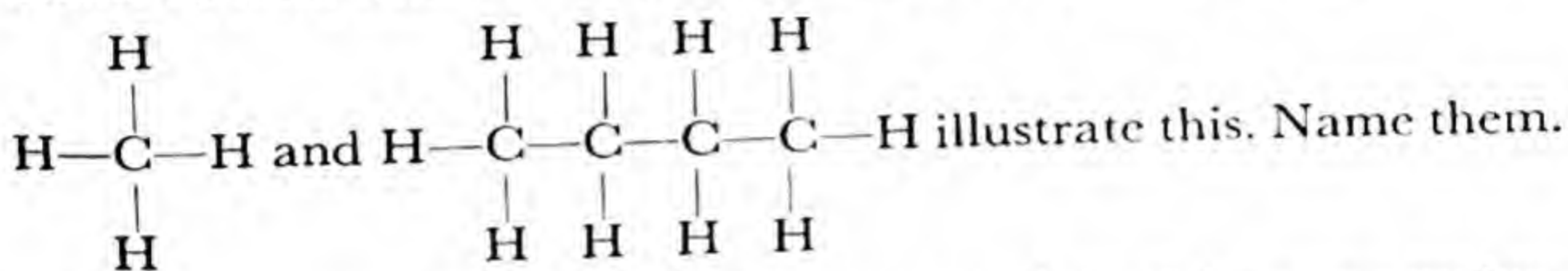
In each series any one member differs from its neighbor by one carbon and two hydrogens (CH₂). This regular progression in molecular weight is the reason for the name, "homologous series." The general formula for the series is useful. For example, in the methane series (so called from the name of its simplest member) we know that a hydrocarbon with five carbons must have twelve

¹ In aliphatic hydrocarbons the carbon atoms are joined in chains, while in the aromatic hydrocarbons (as found in coal-tar distillates) some of the carbon atoms, at least, are joined in rings. The methane series is often called the paraffin series.

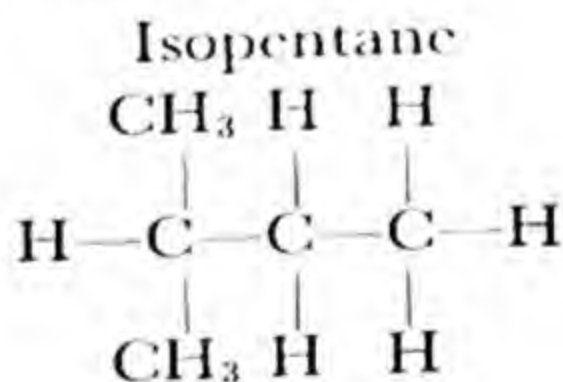
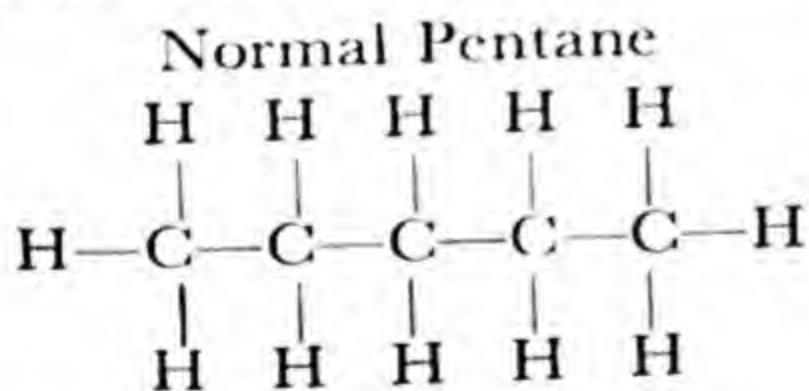
hydrogens in the molecule (C_5H_{12}) because in the series formula (C_nH_{2n+2}), the n is 5 in this case and $2n + 2 = 12$.

The methane and benzene series are by far the most important in the field of organic chemistry if their derivatives are considered. Members of the methane series up to a molecule of 60 carbon atoms are found in petroleum. The first member, CH_4 , makes up about 90 per cent of natural gas. The first four members are gases at ordinary temperatures; from C_5H_{12} to $C_{15}H_{32}$ they are liquids; and from $C_{16}H_{34}$ up they are solids.

The existence of so many compounds of two elements depends wholly on the tetravalence of carbon and the ability of carbon atoms to hold other carbon atoms in long chains or rings.



Isopentane, a branched chain compound, is of the same molecular weight and has the same empirical formula, C_5H_{12} , as normal pentane, a straight-chain compound. The differences in chemical and physical characteristics are due to the manner in which the 5 carbon atoms and 12 hydrogen atoms are combined. The structural formulas of these isomers are:



Exercises

1. Diagram "iso-octane," C_8H_{18} , the standard for rating our present anti-knock motor fuels. Then look at page 597.
2. Isobutane is vital to 100-octane gasoline. Diagram its formula.

It is astounding to learn that although C_4H_{10} has only two isomers, $C_{10}H_{22}$ could have 75 and $C_{14}H_{30}$ could have 1855. Isomeric forms of a compound have the same formula but the atoms are arranged differently (as in normal pentane and isopentane).

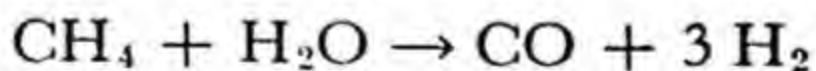
Methane. Methane is formed when many kinds of organic matter are heated out of contact with air. It is often found in coal mines, where it is known as "fire damp," and is thus the cause of dangerous explosions. Petroleum contains some of this substance but the chief source is natural gas, which may contain 85 to 95 per cent of methane, and in rare instances, 98 per cent.

Natural gas is a valuable fuel, yielding carbon dioxide and water on combustion. When 1000 cubic feet of the gas burn, over 10 gallons of water could be collected by chilling the vapors. Natural gas and oil occur in the same fields and, in fact, the gas is really the volatile part of the oil deposit. It is the pressure of reservoirs of this gas that forces oil out in "gushers."

The industry is now so enormous that 4000 billion cubic feet are consumed annually in the United States. Natural gas is an ideal domestic fuel, yet four-fifths of it is used in industry. (How is "carbon black" made? (See page 131.))

As a reserve for winter emergencies Cleveland built three great insulated spheres holding 150,000,000 cubic feet of natural gas, compressed to liquid at very low temperatures. An explosion wrecked one sphere.

Methane, as a raw material, can be used to create a great number of useful products, even liquid fuels for motors. Heated with steam it yields a mixture of hydrogen and carbon monoxide (like water gas, page 91) which can be catalytically converted into other valuable products.

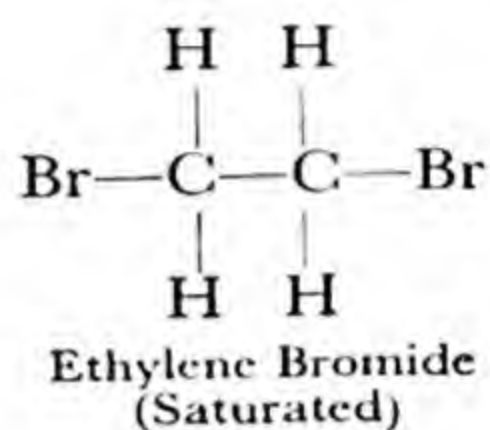
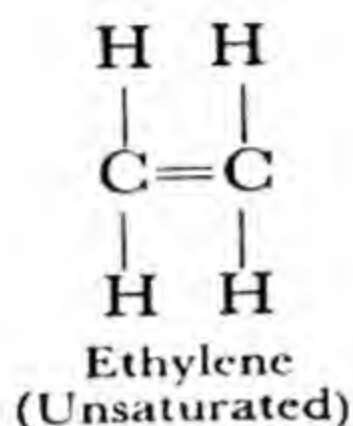
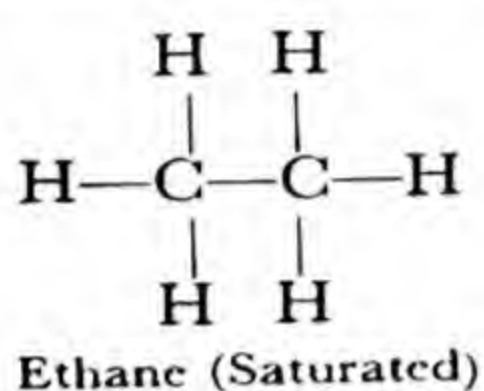


Much cheaper oxygen has made possible an important new development by which natural gas is partially oxidized to yield water gas ($\text{CO} + \text{H}_2$) which can be converted catalytically into gasoline, diesel fuel, alcohols, and acetone (synthol process).

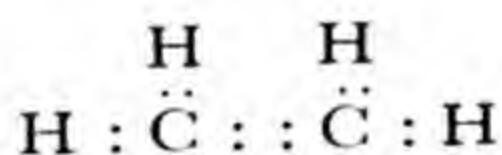
Chlorine derivatives of methane are known and used. Tetra-nitromethane is a terrific explosive, too dangerous to handle.

3. How many grams of oxygen are required to burn 100 liters of methane, both gases being measured under standard conditions?

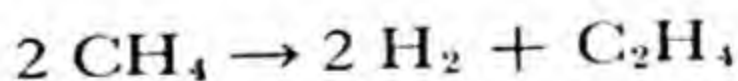
Ethylene, C_2H_4 . This colorless, inflammable gas burns with a luminous flame due to the separation of much incandescent carbon. To its presence (2 per cent in coal gas) is due much of the illuminating power of some commercial gases. It is the first member of a series of unsaturated hydrocarbons. In methane, carbon has its full valence number of four taken up by hydrogen but in ethylene, C_2H_4 , the two carbons are both able to add one monovalent atom (such as bromine). In the structural formula this unsaturated condition may be represented by a double linkage between the carbons. This means only the kind of unsaturation existing in ethylene:



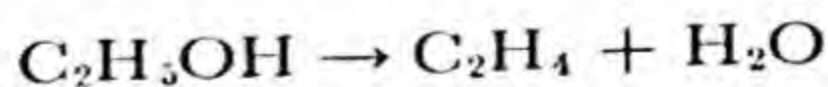
Ethylene may be represented as



As a result of its unsaturation, this compound has an ability to add on bromine and other elements until the usual valence number of four is exercised by the carbon without its "doubling" with itself. When any saturated hydrocarbon is heated strongly in absence of air some ethylene is produced. Even methane can be made to yield it by this thermal cracking or molecule-splitting:

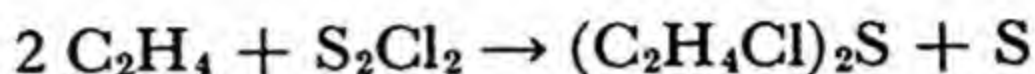


In the laboratory ethylene can be prepared by heating alcohol with concentrated sulfuric acid (a dehydrating effect) or by passing the hot vapors over Al_2O_3 or ThO_2 :

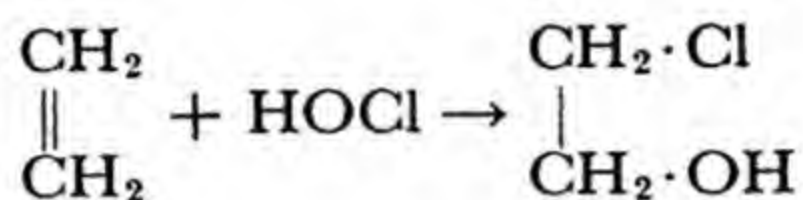


Ethylene is largely used for blow-torch welding and cutting, comparing favorably with acetylene for this purpose and is also valued as an anesthetic and as an aid in the ripening of some fruits.

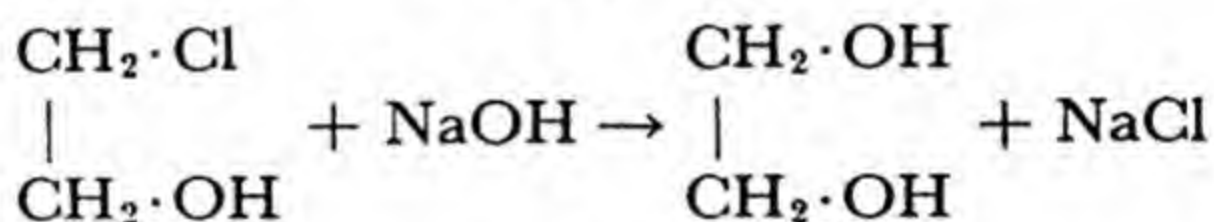
Ethylene reacts readily with sulfur monochloride to form mustard gas, a most effective war gas:



Ethylene passed into chlorine water also reacts, to form ethylene chlorhydrin:



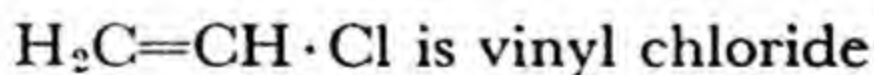
Treated with a base this product yields ethylene glycol, an "anti-freeze" liquid, very similar to glycerine:



A rubber-like product called "Thiokol" is made commercially by converting ethylene into ethylene dichloride which is then treated with a sodium sulfide complex. Polymerization (joining of like molecules to form larger molecules) follows. Ethylene glycol is also nitrated for use in explosives.

Trichlorethylene is a powerful solvent for fats and oils, hence its use, to the extent of 100,000 tons in 1948, in dry cleaning and as a paint remover. The vapors of such chlorinated hydrocarbons are somewhat toxic.

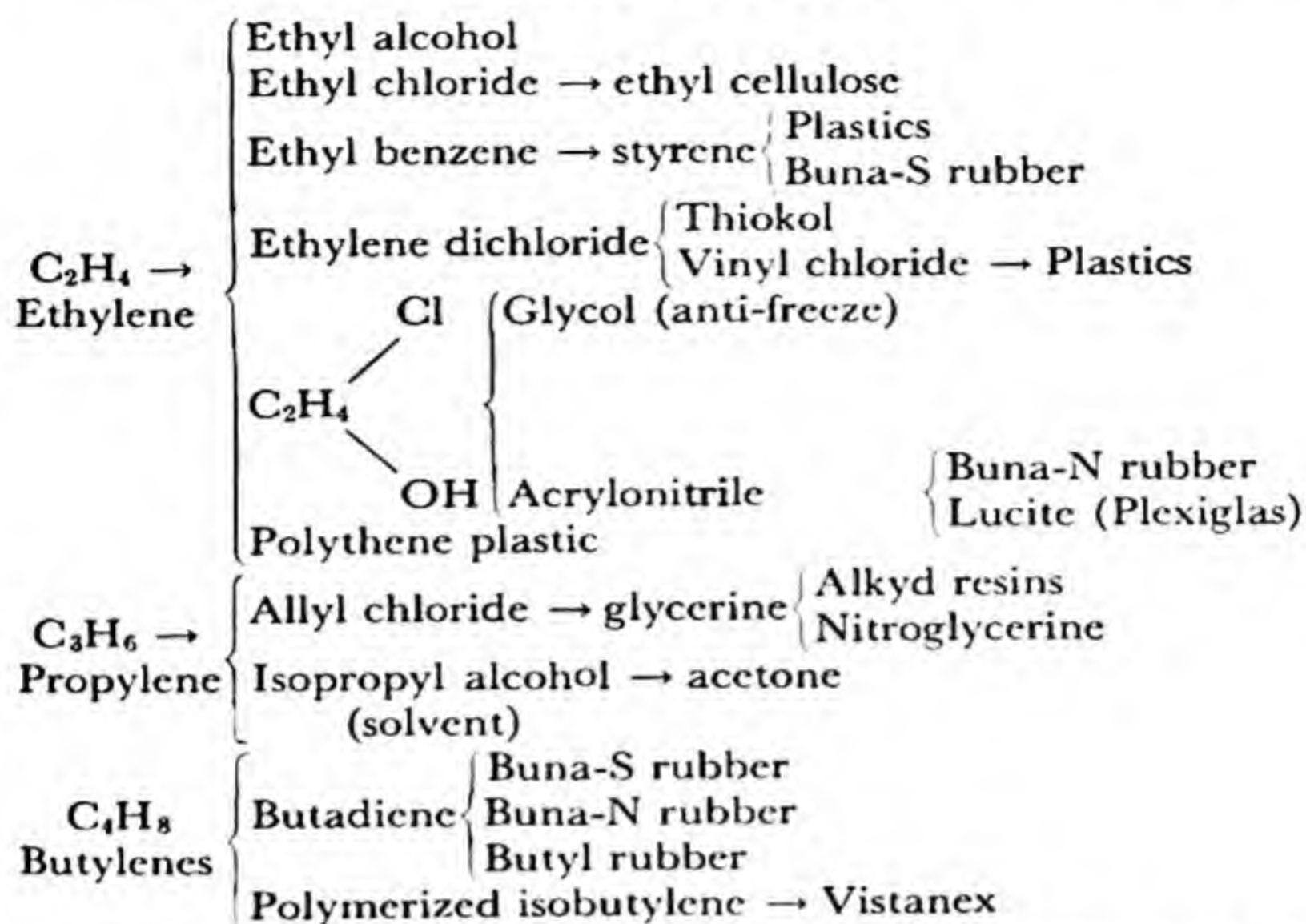
From ethylene we can make derivatives of the vinyl group, the basis of the vinyl plastic industry, although acetylene is generally used as the source of vinyl compounds.



For uses of propylene and butylene see below.

From ethylene we made, in one year, nearly 70,000,000 gallons of ethyl alcohol.

IMPORTANT DERIVATIVES OF SOME UNSATURATED HYDROCARBONS



Acetylene, C_2H_2 . This gas has a lower percentage of hydrogen than ethylene, so it is still more unsaturated. Each carbon is able to add on two bromine atoms or other atoms and become saturated with the usual four valences. The structural formula represents the linkage between the carbons by three bonds, but this is only to be counted as representing the particular degree of unsaturation existing in acetylene, $H-C \equiv C-H$.

The formation of the gas by addition of water to calcium carbide has been given previously ($CaC_2 + 2 H_2O \rightarrow Ca(OH)_2 + C_2H_2$). In a war year Germany used 3,000,000 tons of carbide. Acetylene may also be made by passing natural gas through the electric arc.

Acetylene, fed with oxygen in the acetylene torch, produces an intensely hot flame. (Since acetylene may explode on compression it is always dissolved in acetone when under pressure, for safe use.) With this a 6-inch steel shaft can be cut through in less than a minute and heavy plates are cut with equal speed. As soon as the steel melts it burns in air and is blown away as oxide, in sparks.

Acetylene is the starting point in the synthesis of a large number of organic compounds, some of them of industrial importance. Great quantities of acetic acid are made by catalytic hydration and controlled oxidation in the second stage. The new synthetic rubber, "Neoprene," is derived from acetylene which itself is based upon limestone and coke in the manufacture of calcium carbide (see page 132). Acetylene black, a form of carbon, makes rubber conduct electricity.

Petroleum. Petroleum, varying in color from a light greenish-yellow to a green or reddish-brown, is a mixture of hydrocarbons, although some derivatives containing oxygen, nitrogen, or sulfur may be present. It is sometimes limpid but usually rather viscous.

The early exhaustion of our vast but limited oil reserves, so frequently predicted by scientists and denied by some oil men, is a matter of vital concern. Improvement in refining processes, already startling, and proceeding at a gratifying rate, has the effect of multiplying these resources. Another important factor is the recent deep drilling of oil wells, tapping oil sands hitherto inaccessible. Reserves in sight may be doubled by drilling to 12,500 feet. Such wells cost over a third of a million dollars each.

World Production. Normally the United States produces 70 per cent of the world's annual output of 2,000,000,000 barrels but, as a result of World War II, our production was forced to 1,850,000,000 barrels or more, draining our reserves. The other great oil fields are in Arabia, Russia, Venezuela, Iran and Iraq, the Dutch East Indies, and Mexico. Germany, with no oil, has produced liquid fuel and lubricants from coal by catalytic processes. In the United States we are preparing to do the same thing when need arises.

Refining. Once a simple matter of distillation (separation of the hydrocarbons by their difference in boiling points), petroleum refining has been revolutionized by the demands of the auto industry for gasoline and lubricants. In 1900 kerosene for lamps was the chief product and all the gasoline produced in that year would supply our motor needs for less than one hour today. Gasoline is a mixture of hydrocarbons ranging from C_6H_{14} to $C_{12}H_{26}$. Kerosene hydrocarbons may range from $C_{12}H_{26}$ to $C_{16}H_{34}$.

At present the average yield from 100 gallons of crude petroleum is:

44 gals. gasoline	3 gals. lubricants
36 gals. fuel oils	8 gals. asphalt, wax, coke, etc.
6 gals. kerosene	3 gals. lost

We still get great quantities of paraffin wax (380,000 tons), petroleum asphalt, and coke from the petroleum refinery.

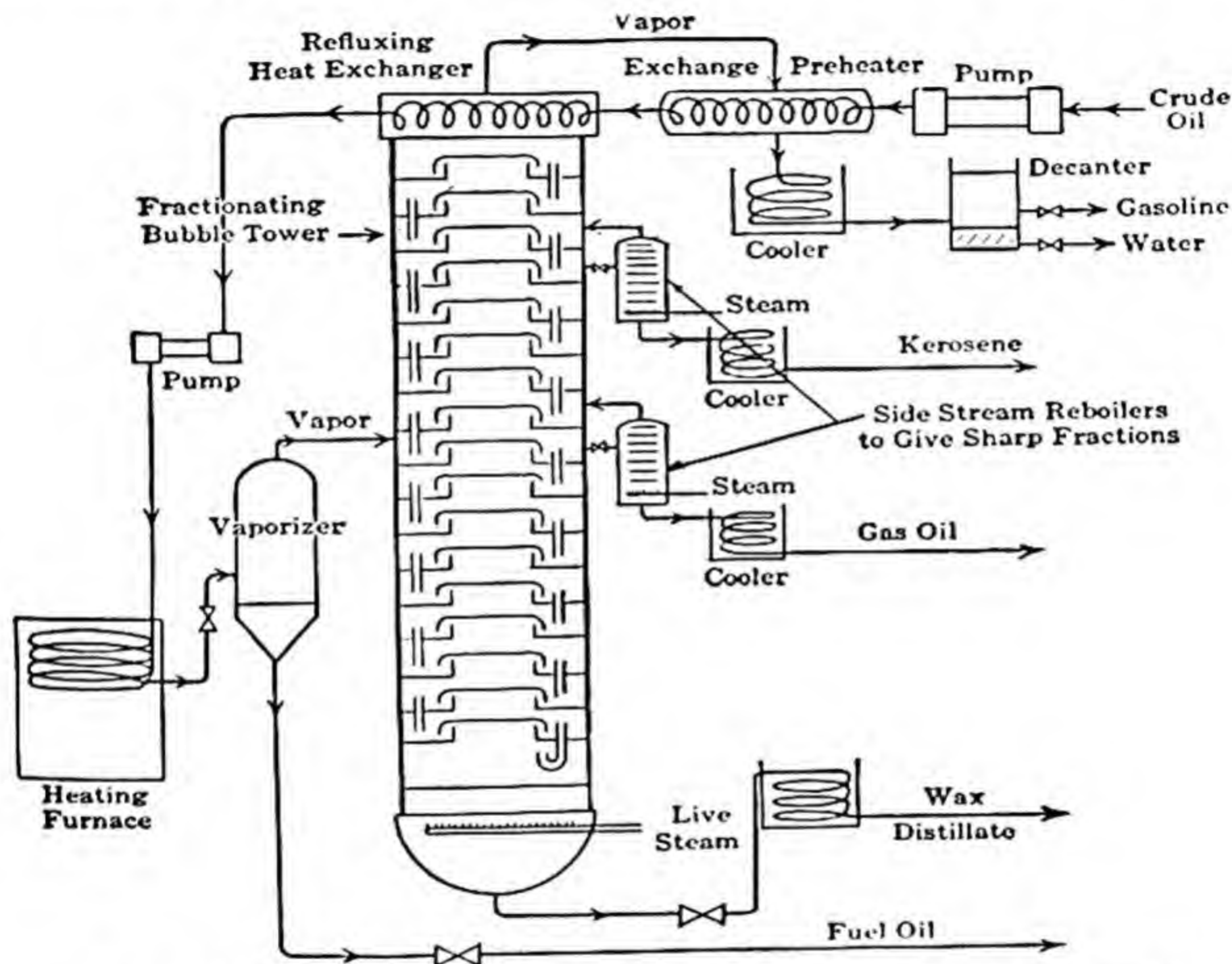


Fig. 156. Petroleum distillation. (From Conant, *Organic Chemistry*.)

The demand for more and better gasoline has introduced such modern improvements on distillation as cracking, hydrogenation, dehydrogenation, polymerization, alkylation, isomerization, and solvent refining.

Cracking. At high temperatures and very great pressures petroleum hydrocarbons are cracked, or split, into smaller molecules with hydrogen as a by-product. Some "reforming" may

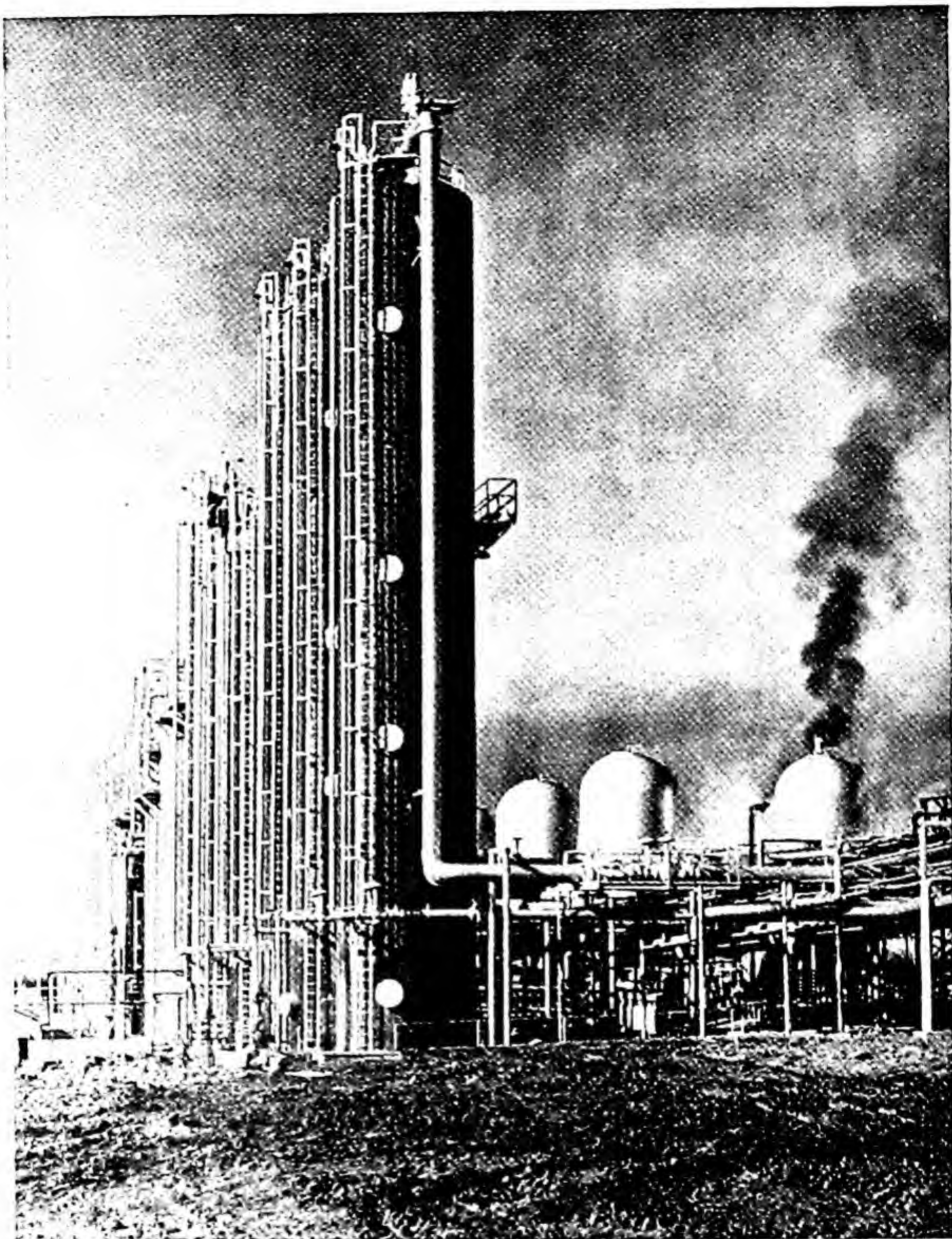


Fig. 157. The modern petroleum refinery is a triumph of chemistry and engineering.
(Courtesy Phillips Petroleum Company.)

take place between the fragments. This splitting of heavier molecules doubles the yield of gasoline (22 per cent) naturally occurring in petroleum. Even peanut and cottonseed oils have been cracked to yield gasoline and Diesel fuel. Catalytic cracking at lower pressure is now the practise.

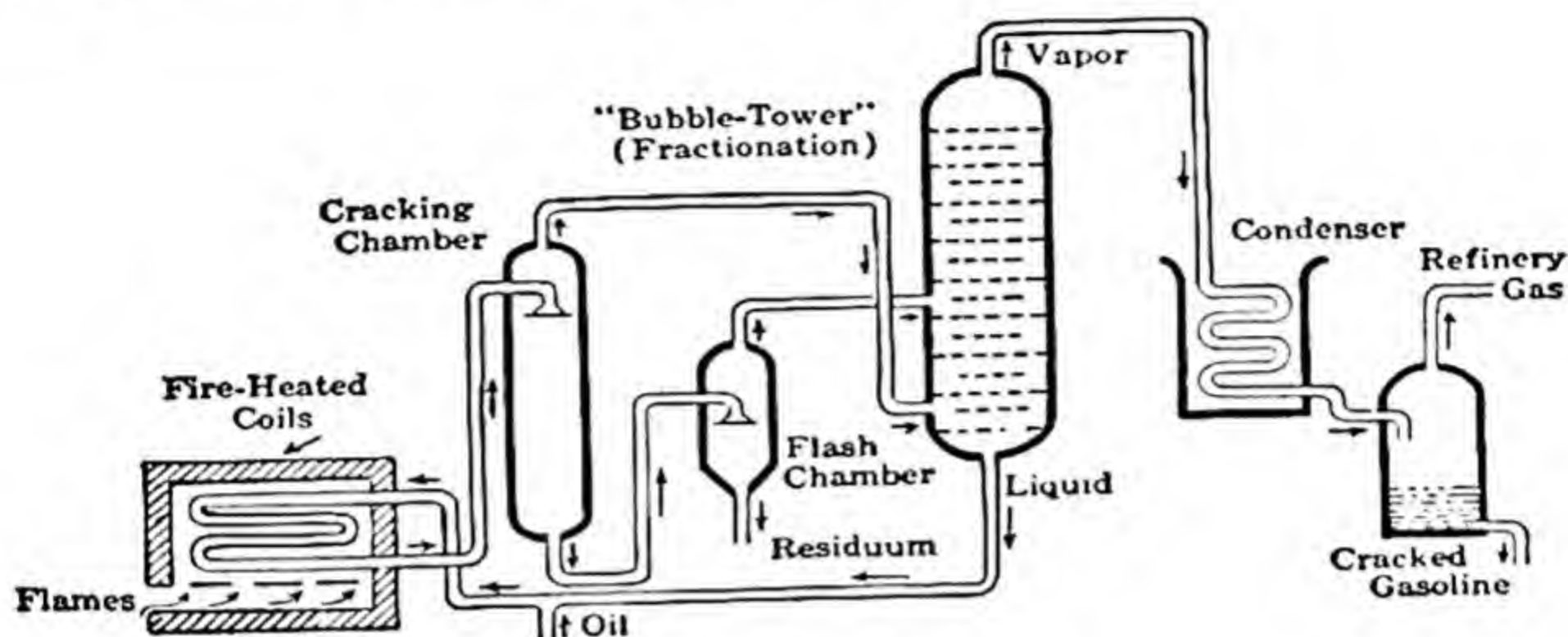


Fig. 158. Petroleum cracking.

Hydrogenation. The unsaturated molecules resulting from the cracking of petroleum fractions can be forced to add hydrogen, thus creating new products. The success of hydrogenation of coal in Germany to yield liquid fuels led to catalytic hydrogenation of petroleum in this country. The gasoline resulting is remarkably low in sulfur compounds and rich in naphthenes and aromatics of excellent anti-knock value. The reaction tubes are built like cannon with alloy steel walls seven inches thick, for they must withstand enormous pressure and temperatures up to 550°C .

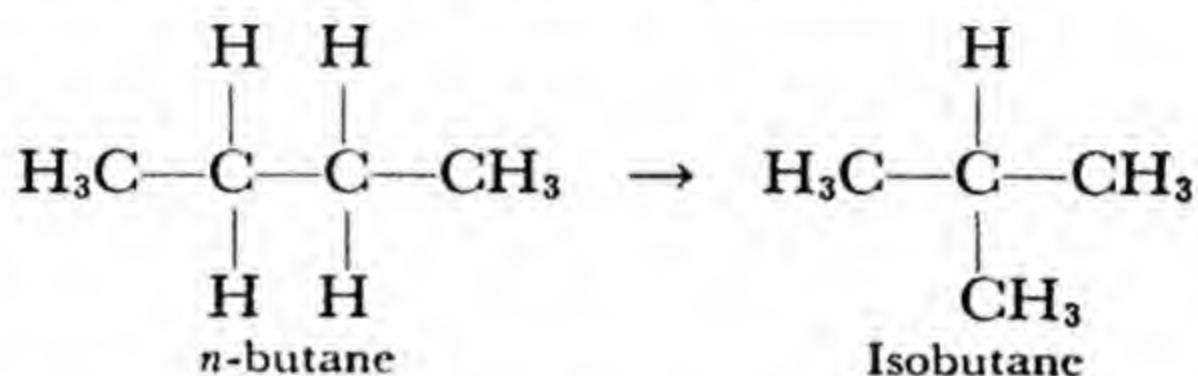
Dehydrogenation. The breaking off of hydrogen atoms from adjacent carbon atoms to produce an unsaturated condition is roughly the opposite of hydrogenation. Normal butane, by dehydrogenation, becomes *n*-butylene, which can be catalytically converted into butadiene for synthetic rubber.

Another remarkable blending agent in production of super fuel is tryptane, 2,2,3-trimethyl butane. Could you diagram its structure, calling the first carbon atom from the end of the chain 2, and the next, 3?

Alkylation. The introduction of "alkyl" groups (CH_3 , C_2H_5 etc.) into a hydrocarbon makes possible neohexane (a valuable blending agent in gasoline), isooctane of high anti-knock rating, and other important derivatives.

A favorite alkylation reaction is that between isobutane and some olefin (unsaturated C_2H_4 , C_3H_6 , C_4H_8 , etc.). The catalyst is usually sulfuric acid or hydrogen fluoride.

Isomerization. The rearrangement of atoms within a hydrocarbon molecule to form an isomer has been put to good use in converting abundant normal butane into isobutane, of which there is not enough. Heat and anhydrous aluminum chloride as catalyst cause the rearrangement of atoms.

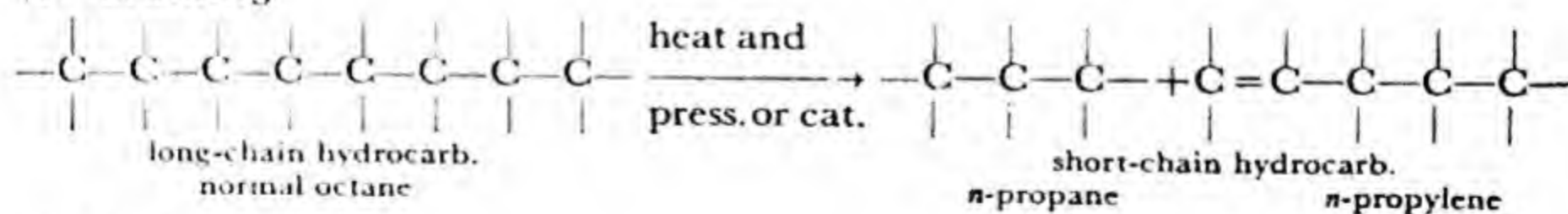


Aromatization. The aliphatic compound, normal (straight-chain) heptane, can be catalytically changed (with some loss of hydrogen) into the closed-ring aromatic compound, toluene. By similar methods normal hexane can be aromatized into benzene. At times the demand for these important aromatics exceeds the supply. The toluene so prepared is our chief source of T.N.T.

4. What other demands are made by the auto industry? Name five.

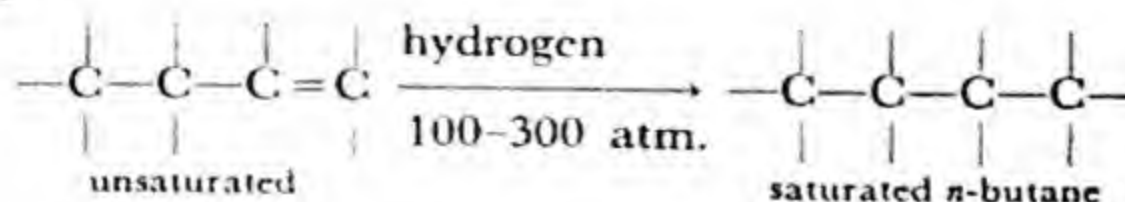
REACTIONS UTILIZED IN THE PETROLEUM REFINERY

(1) Cracking



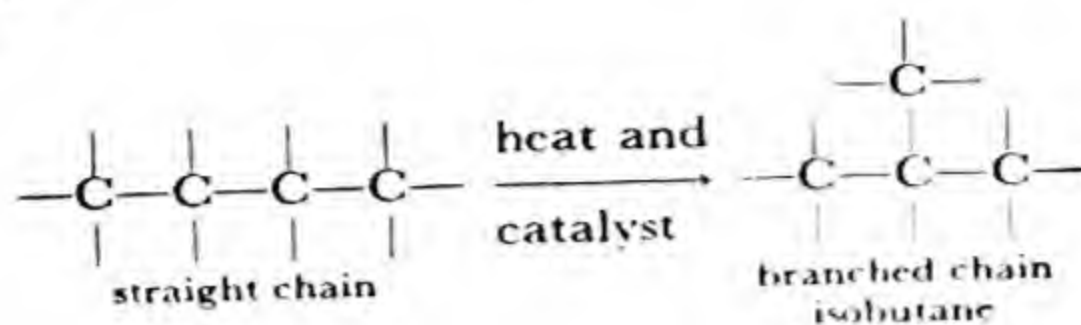
(2) Hydrogenation

n-butylene

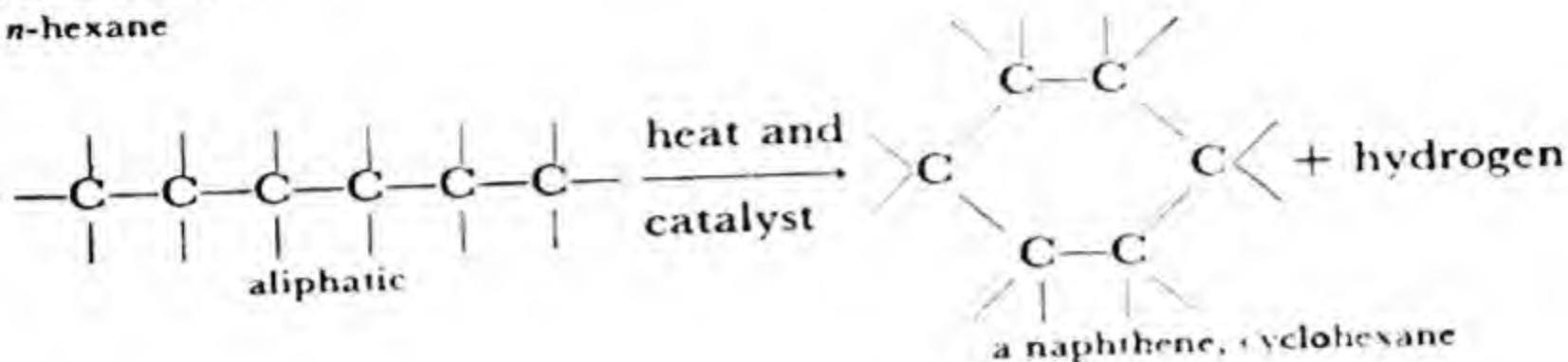


(3) Dehydrogenation Reverse of the above

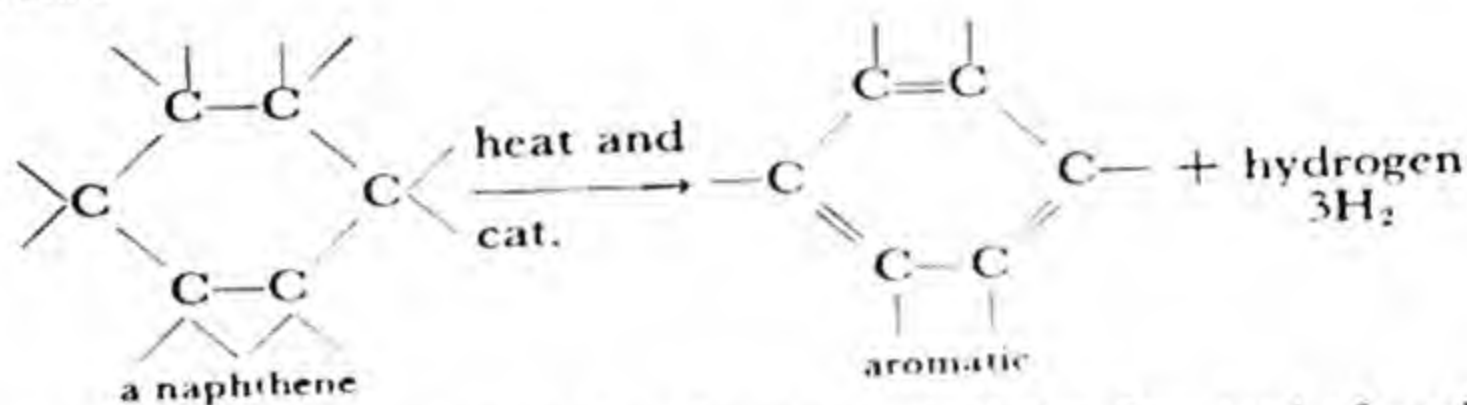
(6) **Isomerization**
n-butane



(7) **Cyclization**
n-hexane



(8) **Aromatization**
cyclohexane



A hydrogen atom is understood to be present at the free end of each line.
(Courtesy M. E. Clark and *Met. & Eng. Chem.*)

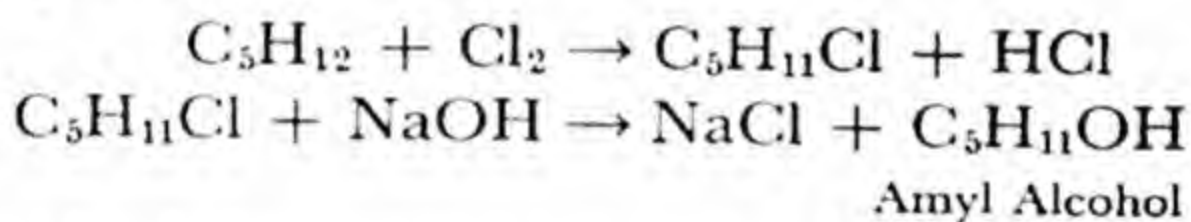
Solvent Refining. At the present time the manufacture of lubricating oils is undergoing a revolution. Losses from use of sulfuric acid in the old method of refining petroleum together with more rigid specifications for lubricants (that have a desired viscosity changing little with temperature, that do not carbonize or gum) led to the rapidly growing use of solvents to remove the last percentage of wax, the naphthenes, and asphalt. Among the numerous solvents are propane (a gas at ordinary pressures and temperature which must be used under considerable pressure), phenol, cresols, liquid sulfur dioxide, dichlorethyl ether, a benzene-acetone mixture, and sulfur dioxide-benzene in varying proportions.

Liquefied propane precipitates troublesome waxes and asphalt from lubricating oil stock. Lubricants extracted with propane are

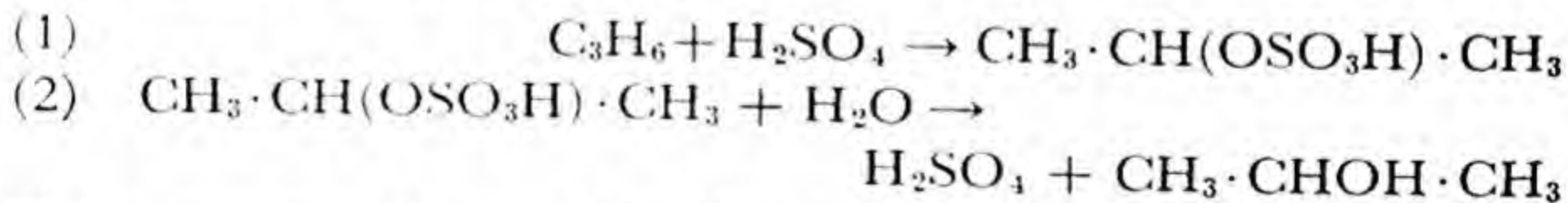
thin enough to permit the starter to turn over a cold motor — and at the same time remain sufficiently viscous in a hot motor for proper lubrication.

Chemicals from Petroleum. A large number of compounds are now being prepared — not merely separated — from petroleum by chemical reactions. In fact we know how to make every known organic compound from methane. Chlorine is the great reagent in attacking aliphatic compounds (natural gas and petroleum) while nitric and sulfuric acids are very effective with the aromatics (coal tar products (benzene, etc.)). The cracking process started this new synthetic chemistry and now hydrogenation, chlorination, polymerization, sulfonation, and other processes add to the possibilities.

For example, the isomeric pentanes stripped from natural gas may be chlorinated to the degree indicated below and the product treated with a base to yield amyl alcohol. This is readily converted into amyl acetate, a valuable solvent used in nitrocellulose lacquers.



Reaction (2), below, represents the hydrolysis of the sulfate formed in (1) from propylene. A similar process for ethyl alcohol is only beginning to be utilized but for several years large quantities of isopropyl alcohol, $\text{C}_3\text{H}_7\text{OH}$, have been made by reactions with refinery propylene, C_3H_6 :



This isopropyl alcohol, $\text{C}_3\text{H}_7\text{OH}$, is a formidable rival in properties to ethyl alcohol. One of the butyl alcohols, similarly prepared in large quantity, is converted into a butyl acetate, an important solvent for the lacquer industry. Hydrocarbons, glycols, alcohols, ketones, ethers, esters, aldehydes, acids, amines, chlorinated compounds, vinyl resins, and their derivatives are possible.

The unsaturated hydrocarbons produced by thermal stripping

of some hydrogen from saturated hydrocarbons are especially useful in the preparation of many needed chemicals. Ethylene comes to mind as a valuable raw material but the propanes can be stripped to yield reactive propylenes and the butanes to yield butylenes. From the butylenes we make butadiene, so fundamental in the manufacture of synthetic rubbers.

Glycerol can be made by regulated chlorination of propene, followed by hydrolysis. This possibility serves as a price control.

We know how to prepare benzene and toluene from *n*-hexane and *n*-heptane with the aid of proper catalysts and temperatures. Both are raw materials for the manufacture of military explosives. One company is now preparing one hundred synthetic chemicals from the ethylene, propylene, and butylenes resulting from modern oil-refinery operation.

Oil Shale. When our petroleum deposits are exhausted we can, if necessary, develop the enormous deposits of oil shale found in Colorado, Utah, Montana, Nevada, California, and Indiana. These are sufficient to last for centuries. The oil does not occur in the shale as such, but is obtained by retort distillation which breaks down complex organic compounds in the shale. Among the distillation products are oils, ammonia, and fuel gas.

The Colorado shale, easily mined, covers an area of 1500 square miles with a possible yield of 24,000,000 barrels of oil to the square mile. This area could furnish 300,000,000 tons of ammonium sulfate — a boon to the farmer. One barrel of oil can be distilled from one ton of shale. Our Government is now operating a pilot plant. By cracking methods, our own shale could be made to last 400 years as a source of motor fuel.

Gasoline from Coal. The Fischer-Tropsch process produces water gas from coal, commercial 90 per cent oxygen and steam, and catalytically converts this mixture into gasoline and diesel fuel. The process is now applied to natural gas.

Catalysis with iron, cobalt, or nickel up to 200 pounds pressure and at 350° F. yields a fuel of 40-octane rating which can be cracked, isomerized, aromatized, and polymerized to give a gasoline of 70-octane rating. This process will supply us with gasoline when petroleum is exhausted, perhaps before.

Coal dust and coal tar have also been hydrogenated catalytically by the Bergius process under 4500 pounds pressure at 500°C . using metallic sulfides as catalysts. After further steps a 70-octane fuel is obtained (one barrel from 0.8 ton of coal).

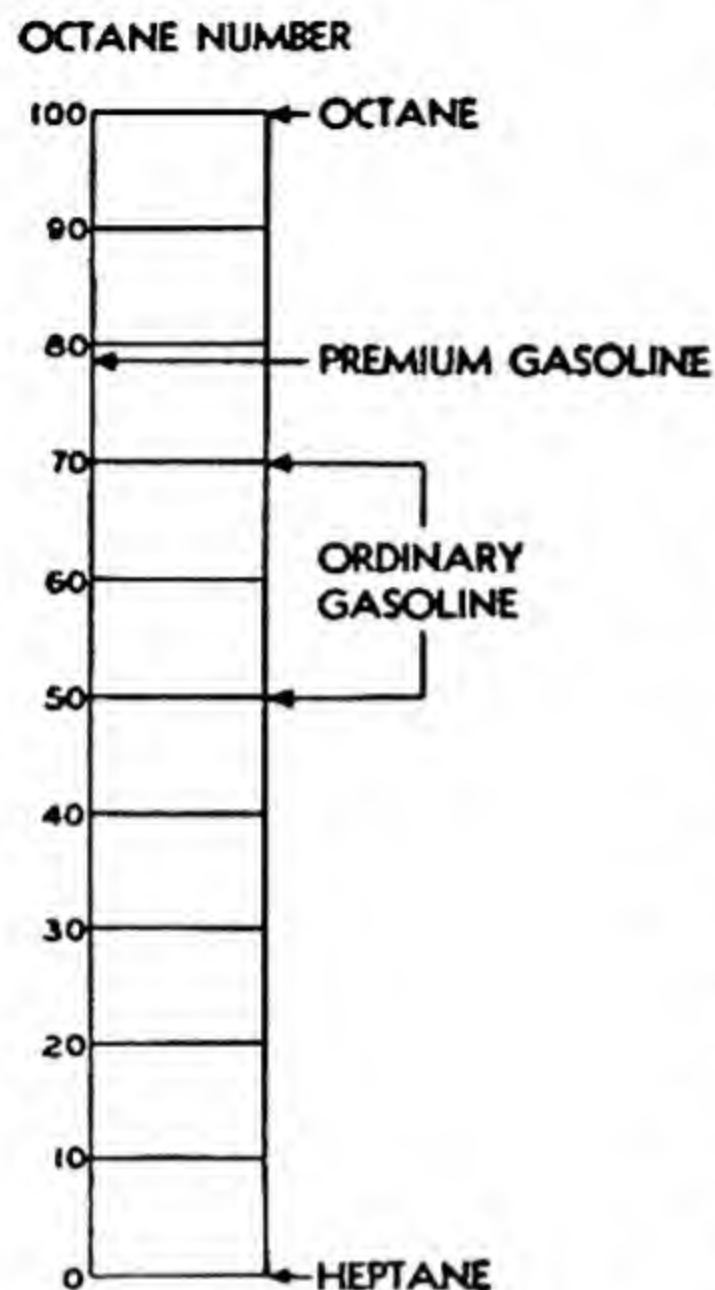


Fig. 159. Octane number of gasoline.

Liquefied Refinery Gases. Propane, C_3H_8 , and butane (or isobutane), C_4H_{10} , have become important by-products of oil refining whereas formerly they were burned under boilers in the plant for steam-making purposes. Now these gases are compressed in steel cylinders or even in tank cars and sold as a convenient source of gaseous fuel for homes outside the city. Small towns are finding it cheaper to distribute this gas through their local mains than to manufacture coal gas or water gas. In 1926 only 465,000 gallons were sold in the United States while in 1948 2,000,000,000 gallons were needed.

5. Using the illustration below as a model continue as indicated. For Liquid Fuel substitute Tin Cans, Houses, Auto Bodies, Airplane Bodies, and Fabrics.

Competition

Old Sources:

Gasoline
Diesel oil
Fuel oil
(from petroleum)

LIQUID FUEL

New Sources:

Hydrogenated and catalyzed liquids from coal
Liquids from catalyzed water gas (coke, steam)
Alcohol, benzene
Fats (when cheap enough)

High-Octane Gasoline. High-octane gasoline is usually a blend of good stock with neohexane (a dimethyl butane), iso-octane, or similar blending agent and, in all cases, tetraethyl lead,

$\text{Pb}(\text{C}_2\text{H}_5)_4$. See page 183 for the effect of lead. High-speed fighting planes require 100-octane fuel which has 25 per cent more power than 90-octane. The cruising range of transport planes is greatly increased by such fuel. Our own production of 100-octane gasoline in 1944 reached 600,000 barrels a day, giving us a tremendous advantage over the enemy. This production required 10,000 tons of $\text{Pb}(\text{C}_2\text{H}_5)_4$ yearly.

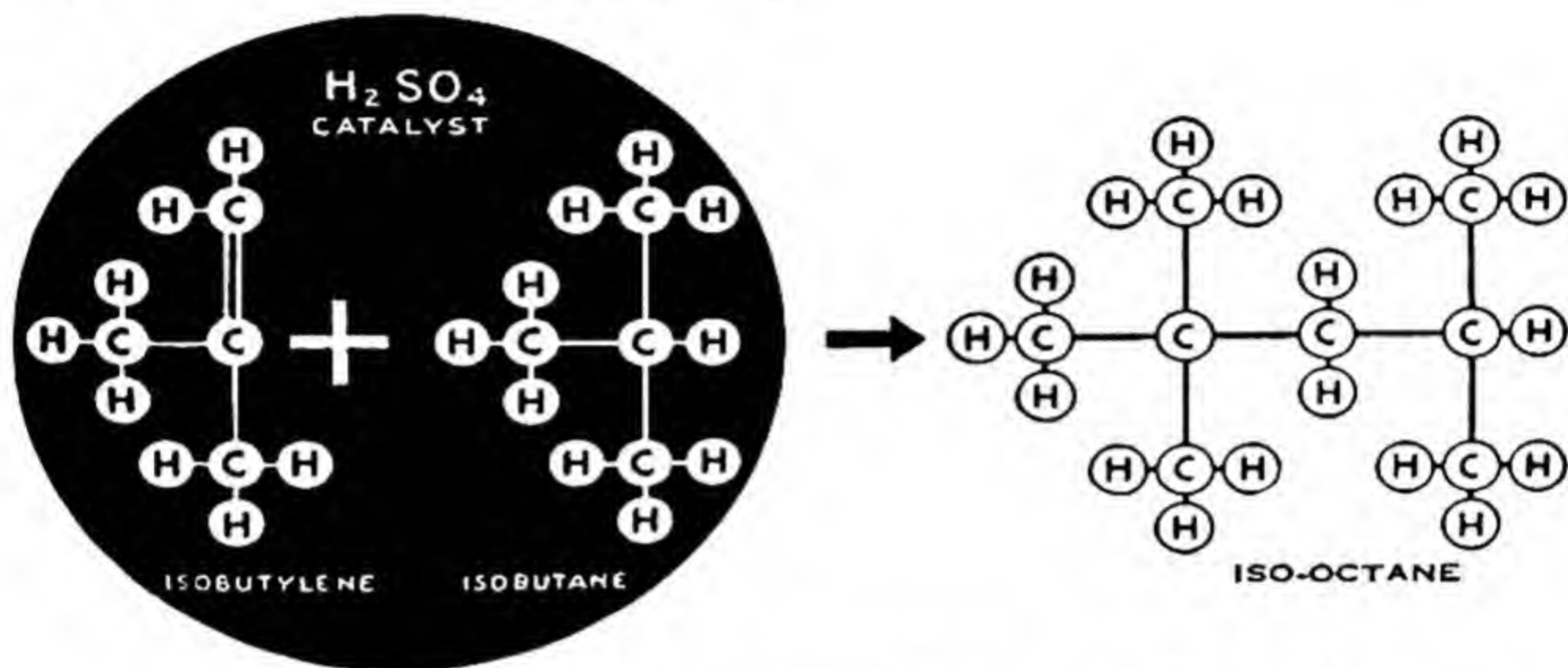


Fig. 160. Iso-octane is made commercially for the swiftest airplanes.

Iso-octane, once a laboratory prize at \$30.00 a gallon, is now produced in great quantity at low cost. Its rating as an anti-knock fuel was set as 100-octane, the standard.

Exercises

6. What were the most valuable petroleum products fifty years ago? What are they today?
7. What will replace petroleum when it is exhausted?
8. What chemical products (steel, etc.) does the motor-car industry use?
9. A candle weighing 80 g. consists of wax composed of 85 per cent carbon and 15 per cent hydrogen. What weight of (a) carbon dioxide and (b) water will be formed by burning 40 per cent of the candle?
10. How many g. of aluminum carbide (Al_4C_3) would react with water to form 83 liters of methane at 15° and 740 mm.?
11. What volume of CO_2 is formed by the combustion of 10 g. of C_2H_2 ?
12. Name several useful substances synthesized from by-products of the petroleum refinery.

13. What type of valence operates in hydrocarbons?
14. Explain cracking, polymerization, and solvent refining of lubricants — as practiced in a modern petroleum refinery.
15. There are three possible isomeric pentanes and these are known (C_5H_{12}). Give their structural formulas, maintaining valences of four for carbon and one for hydrogen.
16. Why are ethylene, propylene, and butylene important?
17. How can a 70-octane gasoline be raised to 100-octane?
18. How can we make gasoline from natural gas? From coal?

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Chapter 52 RUBBER

Columbus observed West Indian natives playing with balls of raw rubber. Later, Priestley, noting that pencil marks could be rubbed out with this strange stuff, called it "rubber." It remained practically useless until 1839 when Charles Goodyear, an American inventor, discovered by heating raw rubber with sulfur that the elastic strength was greatly increased and the warm-weather stickiness and cold-weather brittleness disappeared. He also discovered that on "filling" the rubber and sulfur with certain oxides of lead, it "vulcanized" or reacted with sulfur in much less time and gained better wearing qualities. Thereby he laid the foundations for a billion-dollar industry.

Rubber occurs in the sap or latex of the rubber tree (grown in Brazil and the East Indies), and in many other plants. The latex, a milky emulsion of 32 per cent rubber in water with a little protein, is coagulated (the solids separate from the water) by smok-



Fig. 161. Natives tapping latex from plantation rubber trees in the East Indies. (Courtesy Commercial National Bank and Trust Company of New York.)

ing or by natural souring or by addition of acetic acid. When wild Brazilian trees were the only source the natives used the first two methods, but when 95 per cent of the world's 800,000 tons of raw rubber, of which the United States used 600,000 tons, was obtained from cultivated plantations in the East Indies the acetic acid method was preferred. The coagulated mass is washed, masticated between rollers, and compounded with sulfur and with fillers, such as zinc oxide and fine gas black (carbon black), and with an accelerator to speed up vulcanization. The dough is then molded and heated to about 140°C . The vulcanization now possible in several minutes took three hours or longer without accelerators. It is estimated that the saving to the world in time, equipment, and wear is not less than \$200,000,000 annually — a great service rendered by Oenslager and others by their discovery of accelerators.

It is not to be thought that zinc oxide, carbon black, barium sulfate, white lead, and the other fillers are added merely to cheapen the product. They add strength and wearing qualities to a high degree. A tire made of pure rubber and sulfur would not run a thousand miles. The smaller the particle of a filler the better its effect. We know that rubber is $(\text{C}_5\text{H}_8)_x$, but the chemistry of vulcanization is still in dispute.

It is probable that in natural rubber there are approximately 2000 isoprene, C_5H_8 , molecules linked together, corresponding to a molecular weight of 136,000.

Usually rubber was separated from the natural latex in the East Indies, yet 100,000,000 pounds of latex, preserved with a little ammonia, etc., have been shipped in tankers in a single year to the United States. Sponge rubber is made directly from latex.

Chlorinated rubber and rubber hydrochloride are recent and extremely useful modifications. They are properly classified with Plastics, page 650.

SYNTHETIC RUBBER

Our war with Japan cut off importation from the East Indies of 97 per cent of the 600,000 tons of natural rubber previously

used in a normal year. Since trucks, tanks, jeeps, planes, battle-ships, and hospitals, as well as ordinary motor cars, must have rubber, the war might have been lost but for the rapid development of the very small synthetic rubber industry. Early in 1945 our annual rate of production probably passed the 900,000-ton mark, yet so great was the military need that civilians were allowed very little rubber.

In 1948 we used 355,000 tons of synthetic rubber and 650,000 tons of natural rubber. The demand increases.

The term, "synthetic rubber," is misleading because the several varieties of new products are chemically different from natural rubber. Nor is it fair to call them substitutes, considering that some of them are superior to rubber in resistance to oils, oxidation, and light, while one, at least, is stronger as temperature rises and stands bending better than does natural rubber.

Natural rubber is a polymer (long-chain aggregate) of isoprene, C_5H_8 . Vulcanization involves the reaction of sulfur with the unsaturated isoprene, the sulfur atom serving to tie parallel chains together with increased strength.

Since a number of these synthetic rubbers have as their building brick or unit (the monomer) butadiene, C_4H_6 , which is prepared from petroleum or alcohol or from starch by a special ferment, consideration of synthetic rubbers naturally follows a study of petroleum refining.

A comparison of a few of the several known monomers shows how the chemist imitates and improves on nature.

"MONOMERS," POLYMERIZED INTO CHAINS		COMMERCIAL NAME
Butadiene	$CH_2=CH-CH=CH_2 \rightarrow$	Buna S (aided by styrene), "GRS"
Isoprene	$CH_2=C(CH_3)-CH=CH_2 \rightarrow$	Natural rubber
Chloroprene	$CH_2=CCl-CH=CH_2 \rightarrow$	Neoprene rubber
Acrylonitrile	$CH_2=CH-C\equiv N \rightarrow$	Buna N rubber (aided by butadiene)

Polymerization is brought about by catalysts at the proper temperature. Imitating nature, some manufacturers prepare an emulsion of the monomers in water (similar to natural latex) and carry out polymerization with this mixture. National independence of East Indian rubber is possible whenever that supply is cut off.

Synthetic rubber is now being vulcanized at 14° F. or below instead of the usual 122° F. in order to give tire treads considerably increased wear.

Natural rubber is more elastic, stretches better, and does not readily overheat in heavy truck tires, whereas many synthetic rubbers are more resistant to oils, air, light, and to many chemicals. However, the synthetics are more difficult to fabricate.

Buna S (also called GR-S), polymerized from a mixture of three parts butadiene and one part styrene, is excellent material for tires except for those used in rough service on heavy trucks. It is being improved.

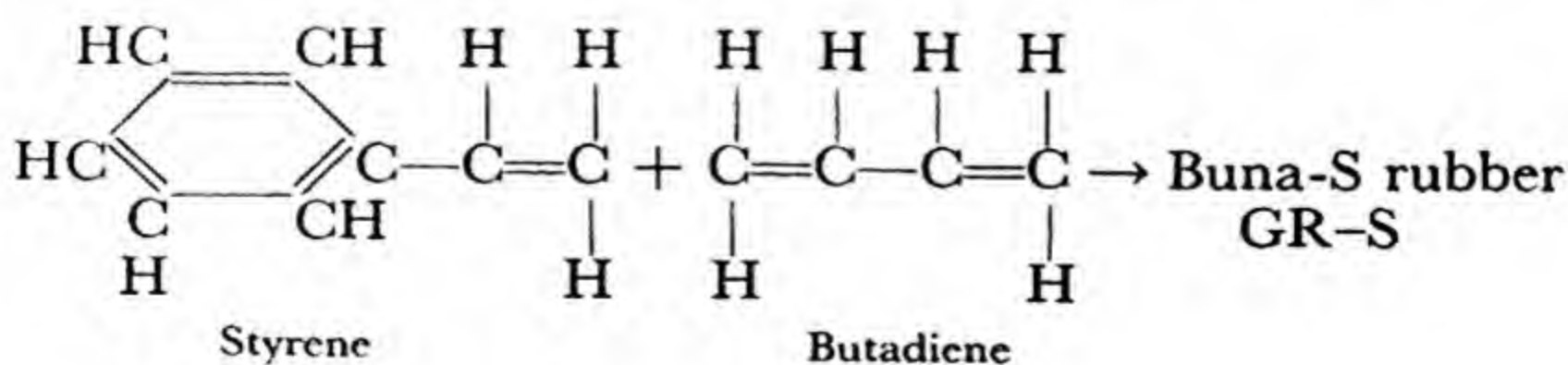
Neoprene, in limited production for several years before World War II, has remarkable oil resistance and excellent abrasion resistance. It is derived from acetylene, C_2H_2 (page 587).

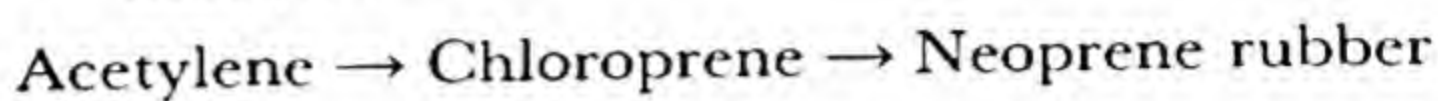
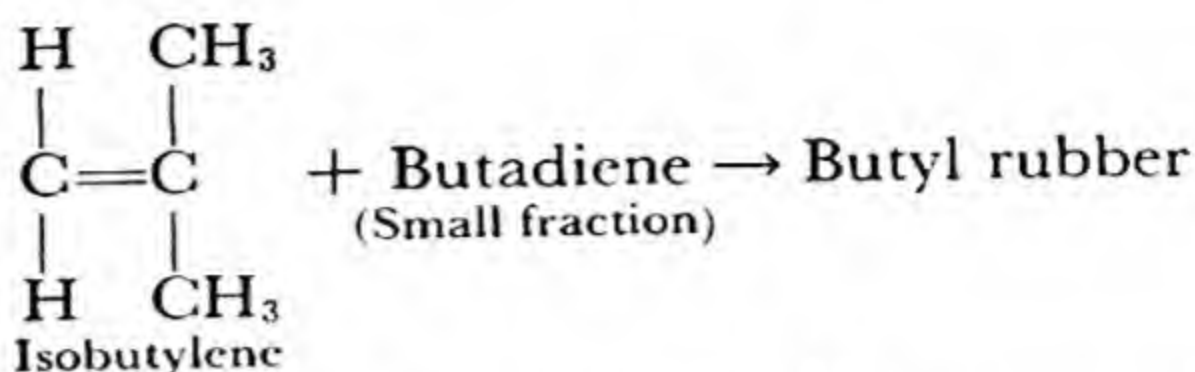
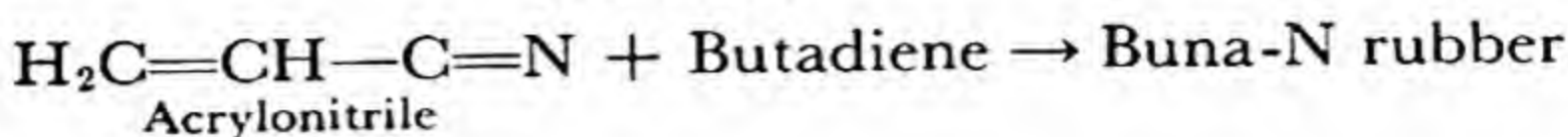
Butyl rubber, product of the petroleum refinery, using isobutylene and a very little butadiene as units for polymerization, makes excellent inner tubes that hold air better than natural rubber.

We have the necessary raw materials for all these synthetics. Butadiene is derived from butane or butylene of the oil refinery; styrene from benzene and ethylene; acrylonitrile from acetylene or ethylene.

A number of flexible plastics such as Koroseal, Pliofilm, Thiokol, Vistanex, and others can substitute for rubber in products other than tires.

Most hose for delivering gasoline or spray lacquers is lined with synthetic rubber because of its superior resistance to deterioration. Bullet-proof fuel tanks in planes are lined with neoprene but between this layer and the outer one is a layer of raw natural rubber or of Perbunan synthetic which swells in contact with leaking gasoline and seals the puncture.





Rubber Competition. The price of natural rubber has fluctuated from \$1.23 per pound in 1918 to \$0.03 in 1932. The success of synthetic rubbers has been of great economic service in eliminating such price fluctuation — and has made us independent of foreign sources. In 1946 synthetic GR-S could be sold for 18.5 cents per pound and it will, with the rapid technical progress being made, soon sell for less. Natural rubber currently is priced at 20 cents but, as plantations are restored, it may be expected to drop considerably in price. The world could make 3,000,000 tons yearly with present capacity of synthetics yet needs only half that tonnage of all rubbers. Both types will have large use because tires, in this country at least, may have synthetic treads (abrasion resistant), natural rubber carcasses (side walls), and butyl rubber inner tubes (best air retention). Flexing of natural rubber side walls produces less heat (and destruction) than is the case with side walls of the synthetic material.

Exercises

1. Are the synthetic rubbers chemically the same as natural rubber?
2. What are the raw materials used in making Buna S? Neoprene? Butyl?
3. What monomer has nature polymerized to make natural rubber?
4. What are the sources of butadiene?

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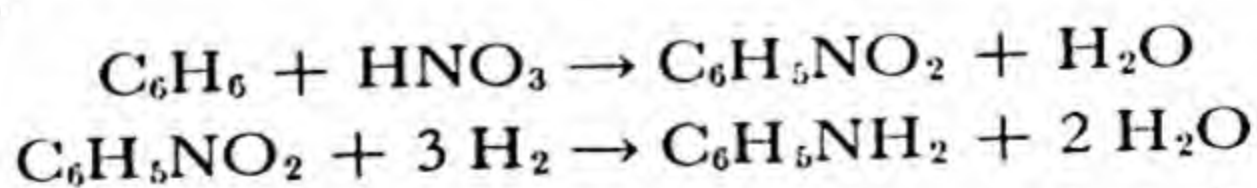
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Chapter 53 THE AROMATIC HYDROCARBONS. FUELS

The aromatic compounds, with carbon atoms connected in rings instead of chains, react more readily with nitric and sulfuric acids than the aliphatic compounds, hence their derivatives were developed first. However in the last quarter century intensive research in petroleum chemistry has had remarkable success.

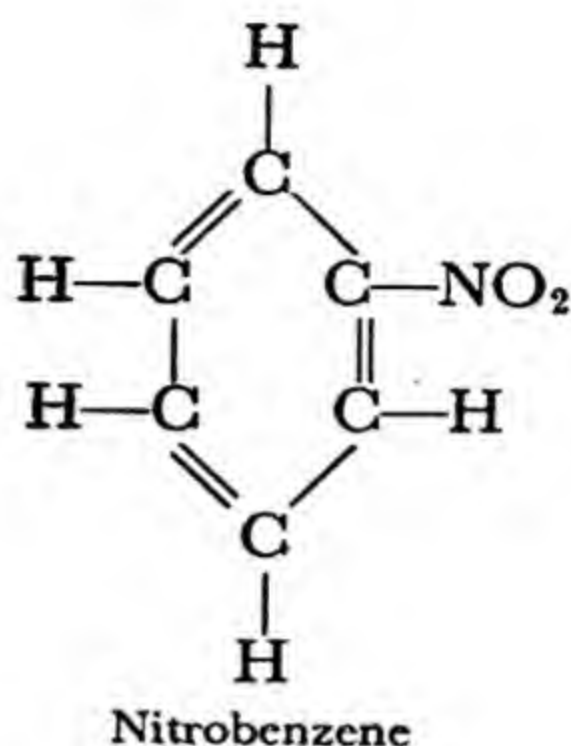
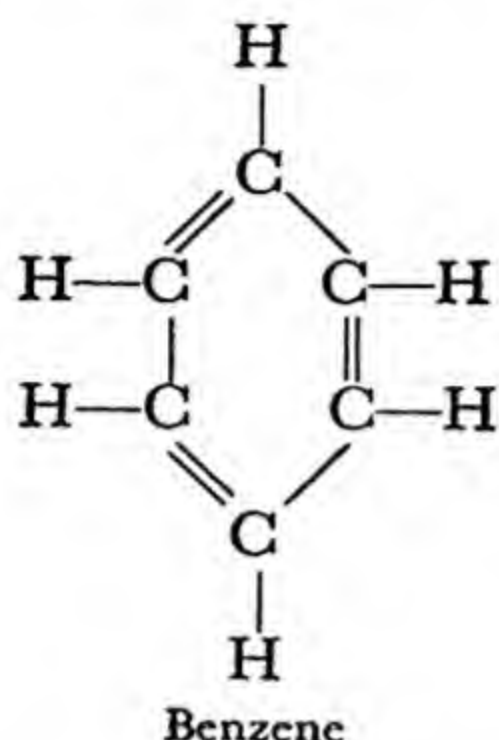
Benzene, C_6H_6 , and Its Series. Benzene was discovered in 1825 by Faraday, and about twenty years later was found by A. W. Hofmann in the gases distilled from coal. It is a colorless liquid, lighter than water and insoluble in water, of a slight odor (not unpleasant), melting at 6° , boiling at 80.4° . It burns with a smoky flame and is an excellent solvent for grease, resins, and rubber. It has long been used in paint and varnish removers and in the manufacture of artificial leather. Benzene vapors are toxic.

Chemically benzene must be classed as an unsaturated hydrocarbon, since it is capable of adding on six hydrogen atoms or six bromine atoms per molecule. But it reacts with nitric acid by substitution to form nitrobenzene, $C_6H_5NO_2$, and this in turn is reduced by active hydrogen to aniline, $C_6H_5NH_2$, the mother substance of a host of beautiful "aniline dyes." It can also be attacked by hot concentrated sulfuric acid and other reagents. In fact nearly one-half of all carbon compounds are derivatives of benzene:

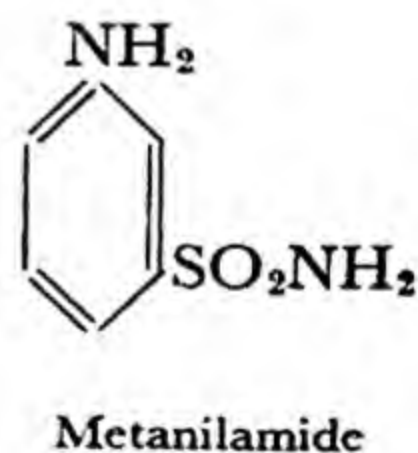
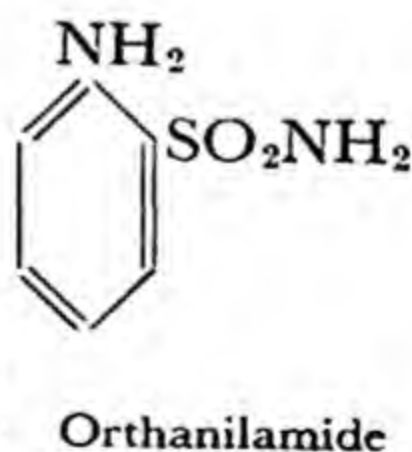
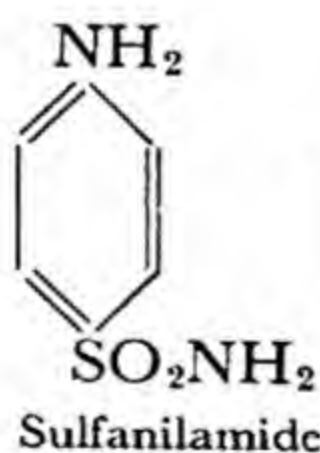
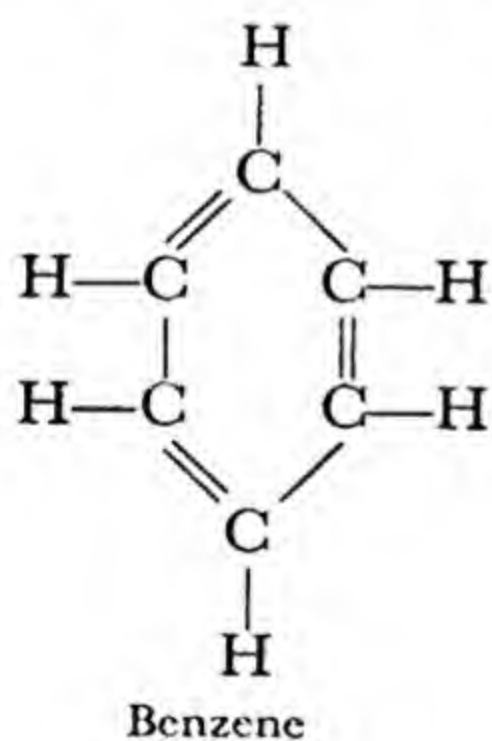


A very interesting line of evidence shows us that the six atoms of benzene are tied together in a ring, very different from the

chains of carbons in the methane series. A comparison of a few structural formulas of benzene and its derivatives will be worth while:



The influence of position of groups in the benzene ring is well illustrated by the powerful medicine sulfanilamide and its physiologically inactive isomers, orthanilamide and metanilamide:



In the abbreviated formulas for these compounds the CH groups of the ring are merely understood, for the sake of emphasis.

Our 150,000,000 gallons of benzene (benzol, as the public calls it) are consumed as an anti-knock addition to our motor fuels and as raw material for manufacture of dyes, medicines, etc.

Toluene, $C_6H_5 \cdot CH_3$. This colorless liquid, boiling at 110° , is

closely associated with benzene in its manufacture from bituminous coal and closely resembles benzene in many properties. Its special interest to the public is as the source of one of the world's greatest explosives, "TNT" (trinitrotoluene).

Our supply of toluene from coal distillation (coke ovens) is quite inadequate for a major war, so it is fortunate that we have learned how to prepare it in much larger amounts from petroleum:

Coal Tar. The most modern coke ovens consist of banks of narrow brick chambers each about 40 feet long, 10 feet high, and 1.5 feet wide. Each chamber holds 12–18 tons of bituminous coal. The ovens are separated by a series of vertical flues in which gas is burned to furnish the heat for coking. The newest ovens coke the charge in 17 hours. Now 97 per cent of our coke is made in these by-product ovens.

The volatile products are washed with water to catch ammonia and some tar, and with heavy oil to catch most of the benzene and toluene. (The ammonia is first absorbed in wash water from which it is afterwards driven off by addition of lime and the passage of steam through the liquor.) The tar is condensed and the remaining coal gas finally purified for use as a fuel. Coal tar is a black, disagreeable mass, but compounds recovered from it are used to make the most delicate colors the world ever saw and some of the most beneficial medicines as well as dainty perfumes. The blackness is due to free carbon. On redistilling the tar the following products, given in order of volatility, are obtained:

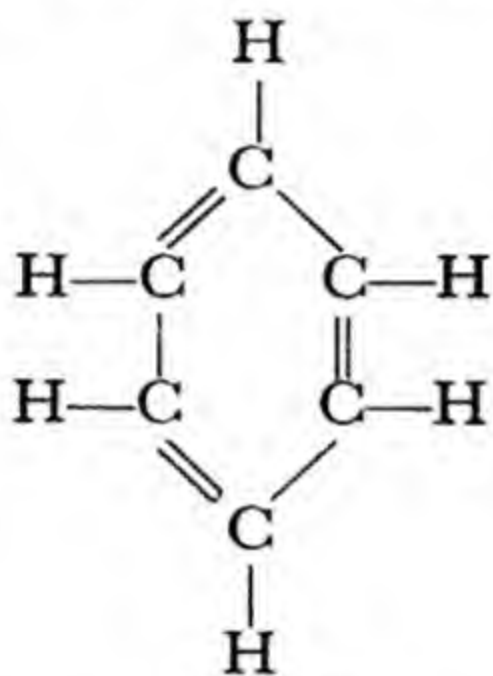
1. Light oil containing a small part of the benzene and toluene
2. Middle oil containing phenol (carbolic acid)
3. Heavy oil containing creosote
4. Anthracene oil
5. Residue of pitch

The residue after distillation may be a sort of asphalt and even petroleum coke. A year's production of petroleum asphalt, rival to natural asphalt, may be 4,000,000 tons.

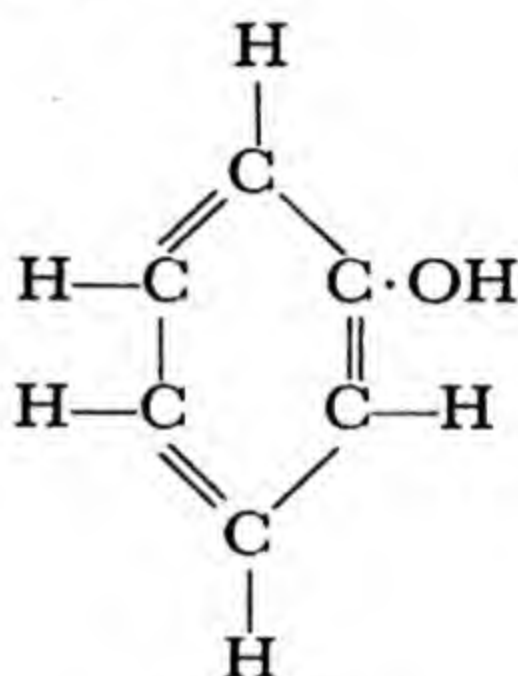
The middle oil yields carbolic acid (phenol) used as a disinfectant and as a source of the explosive, picric acid (trinitrophenol). Road building usually requires 200,000,000 gallons of tar annually.

Phenol. The phenol resulting directly from distillation of coal is insufficient for our needs of 300,000,000 pounds per year so more is produced by the treatment of benzene with sulfuric acid followed by alkaline fusion to introduce the hydroxyl group. However, the major process is the conversion of monochlorobenzene, $C_6H_5 \cdot Cl$, into phenol.

Phenol is important since it reacts with formaldehyde to yield the important plastic, bakelite (see page 650).



Benzene



Phenol

The heavy oil or creosote (phenolic type), is in great demand as a wood preservative for railroad ties, etc.

FUEL GASES

Coal Gas. This most volatile fraction of the distillation of "soft" coal is a valuable fuel. It is largely hydrogen and methane, with a little ethylene, benzene, etc. Its composition varies with the coal and the temperature and the rapidity of coking. Higher temperatures favor decomposition of the hydrocarbons, increasing the percentage of hydrogen and reducing the illuminating power, but greatly increasing the volume of gas. Nearly half this gas is used to heat the retorts but, where the local market justifies it, the cheaper producer gas may be used for retort heating, thus releasing the entire output of coal gas for the market.

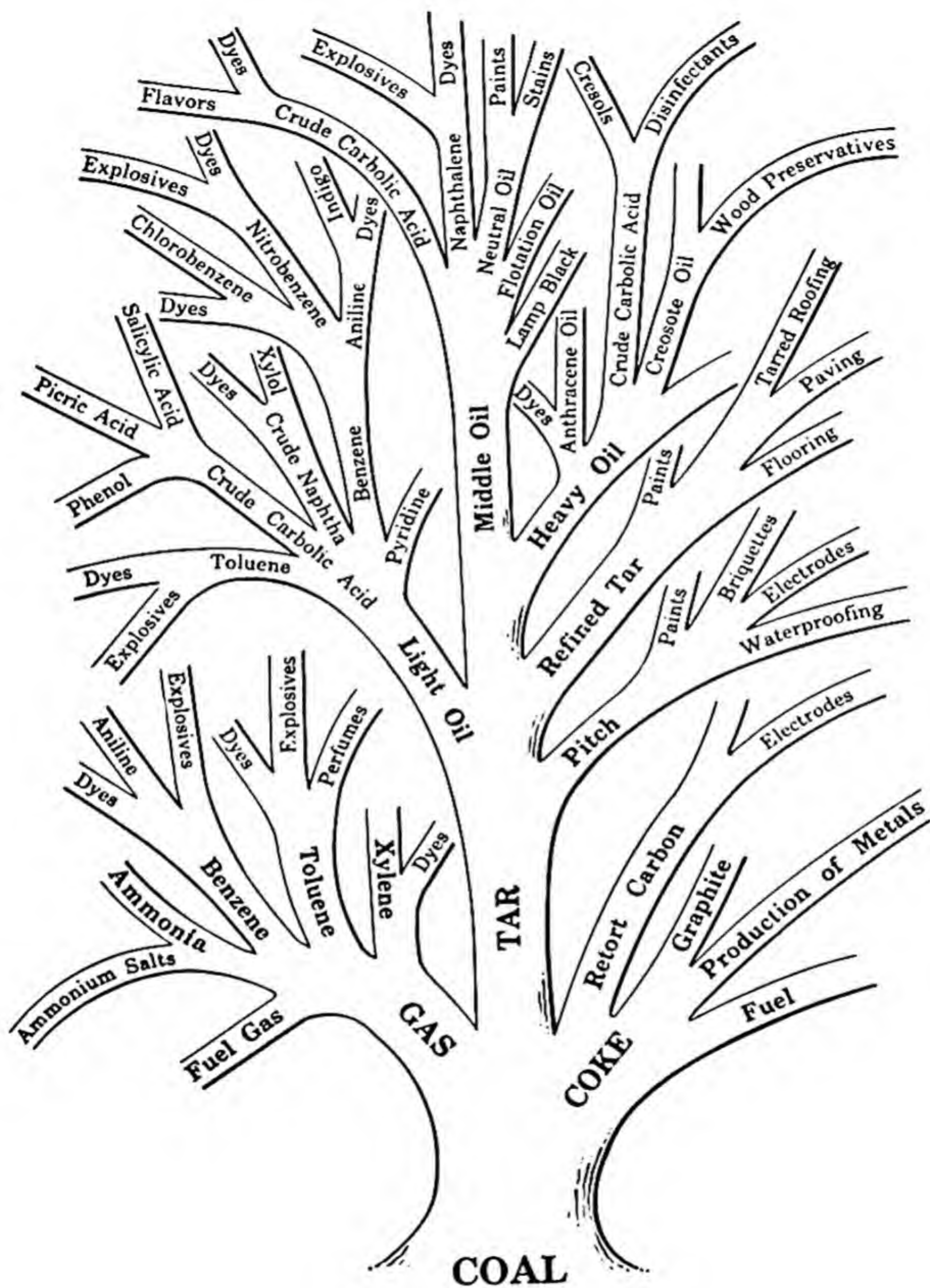


Fig. 162. Coal-tar tree.

Water Gas. Water gas is prepared by burning coke with a forced draft of air until the bed of coke is almost white-hot (Fig. 163). The carbon dioxide formed is allowed to waste. Next, the air is shut off and steam is forced through the coke for five or six minutes. At about 1000° the reaction proceeds, but when the

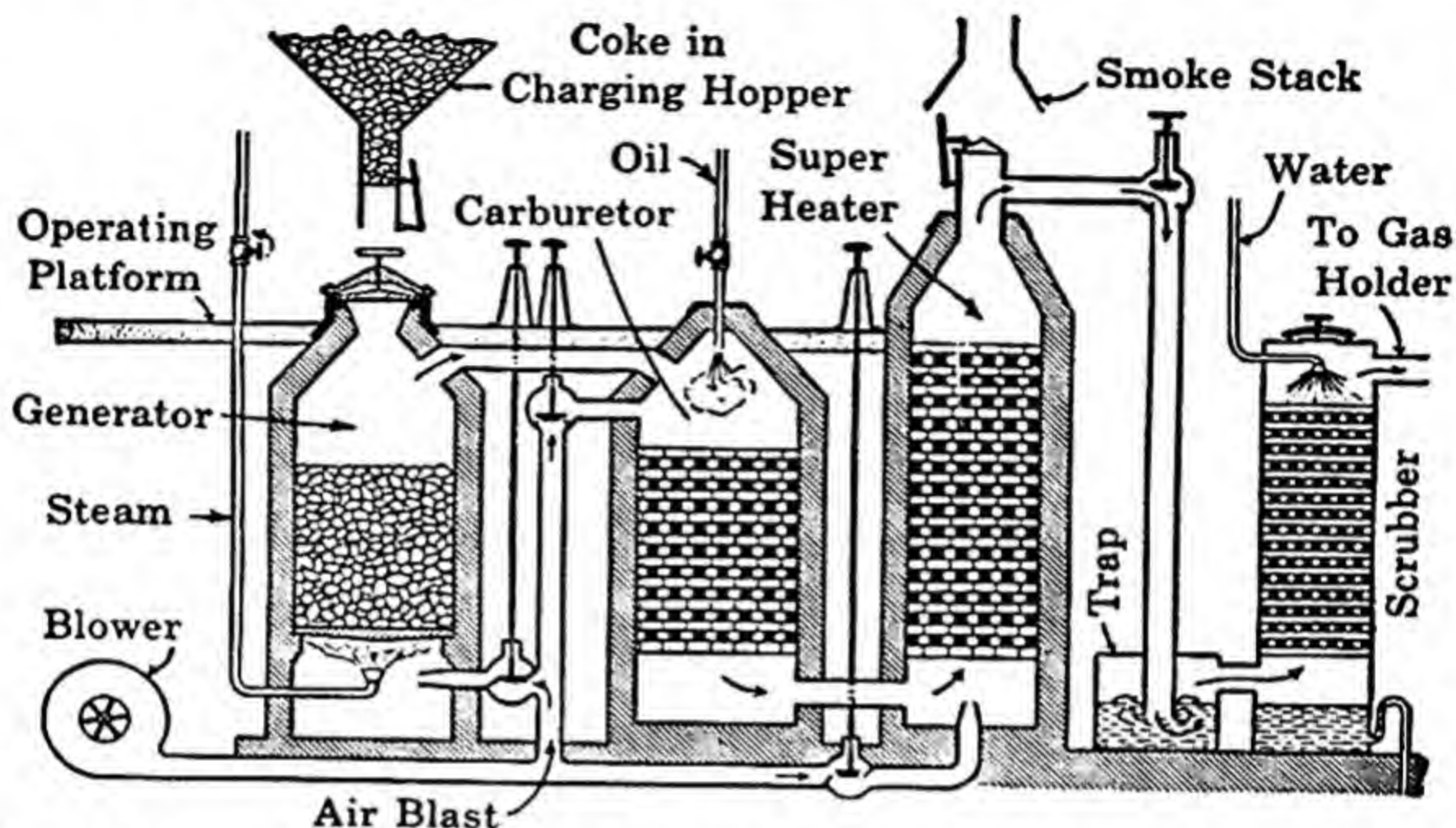


Fig. 163. Water gas. (From Blanchard and Wade, *Foundations of Chemistry*. Copyright. By arrangement with American Book Company, Publishers.)

coke falls much below this temperature the reaction stops. The steam is then shut off and air turned on until the coke is again nearly white-hot. The generation of water gas is intermittent:



This gas is used for domestic cooking and lighting by some cities, although coal gas and natural gas compete. Water gas is extremely poisonous before burning, due to its carbon monoxide content, so small leaks in flexible gas-tube connections are dangerous. Why are its products of combustion non-poisonous?

Water gas is a raw material for the manufacture of methyl alcohol and synthetic liquid fuels and is the American source of hydrogen used in making ammonia.

Producer Gas. In a bed of coal five or six feet deep, the lower layers may be red-hot while the upper layers are not burning at all, possibly only suffering distillation of their volatile matter.

If no flame plays over the surface, the escaping gas has good fuel value. Carbon dioxide formed in the lower layers is reduced, by the excess of hot carbon above, to the valuable carbon monoxide. Some coal gas is distilled from the coal in the upper layers. All the nitrogen of the air used is found in the producer gas, making up nearly half its volume, hence the heating value is low — but the cost is also low. The best economy is to use this gas while it is still hot, thus saving all its sensible heat. In other words, it does not pay to pipe it for a distance. Even lignite can be converted into producer gas.

A “semi-water gas” is made by blowing some steam with the air through the deep fuel bed in the producer-gas process. Reaction with the steam adds hydrogen from the water and more carbon monoxide.

In times when gasoline was scarce in certain countries thousands of “gasogene” or charcoal-burning devices were used to furnish fuel to propel motor vehicles. With a regulated air supply carbon monoxide or, if some steam was introduced, a water-gas mixture resulted. This gaseous fuel was then exploded in the motor cylinders.

Blast Furnace Gas. This is a sort of producer gas taken from the top of a blast furnace used in iron making. Here we have a blast of air rising through a deep bed of coke and iron oxide. The product is a mixture of nitrogen, carbon dioxide, and carbon monoxide. About one-fourth of the mixture has fuel value and it is used in the plant to operate gas engines or to generate steam.

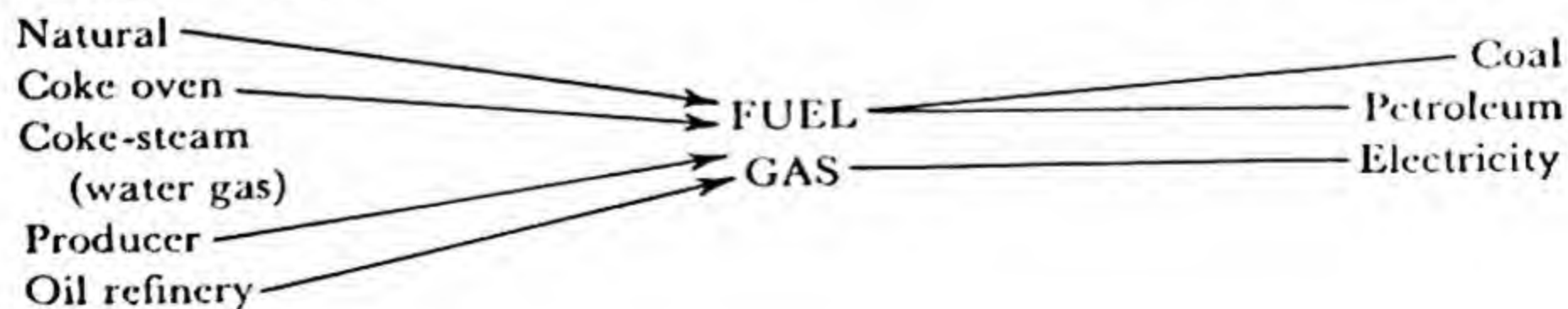
Oil Gas. Petroleum distillates may be “cracked,” by heating them in the absence of air, to form fuel and illuminating gases. Such products are known as “pintsch gas,” “blau gas,” etc.

Natural Gas and Liquefied Oil Gas. See pages 584 and 596.

Competition

Processes to make:

In competition with:



Energy Sources. In 1920 coal furnished 80 per cent of the United States' energy requirements. By 1947 the proportion was 47 per cent from coal, 30 per cent from petroleum, 10 per cent from natural gas and 12 per cent from hydroelectric sources. The future will owe much to atomic power and, perhaps, to gas generated at the coal mines.

Flames. The shape of a flame is determined by the boundary between two gases which are reacting with the evolution of light and heat. It does not matter whether a jet of hydrogen burns in an atmosphere of oxygen or a jet of oxygen burns in an atmosphere of hydrogen. The shape of the flame and the products are

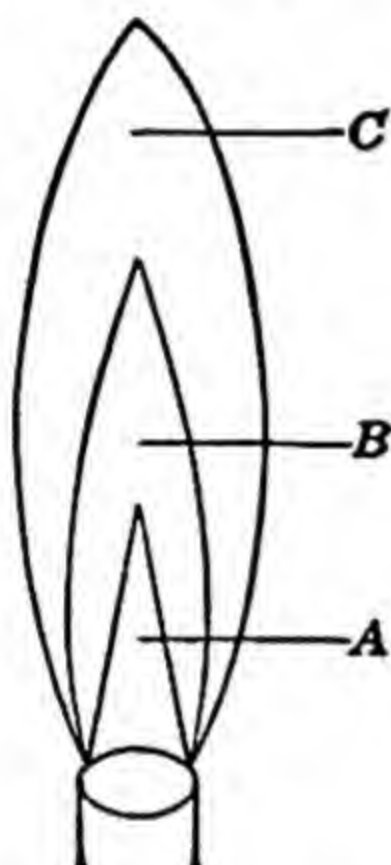


Fig. 164. Flame zones.

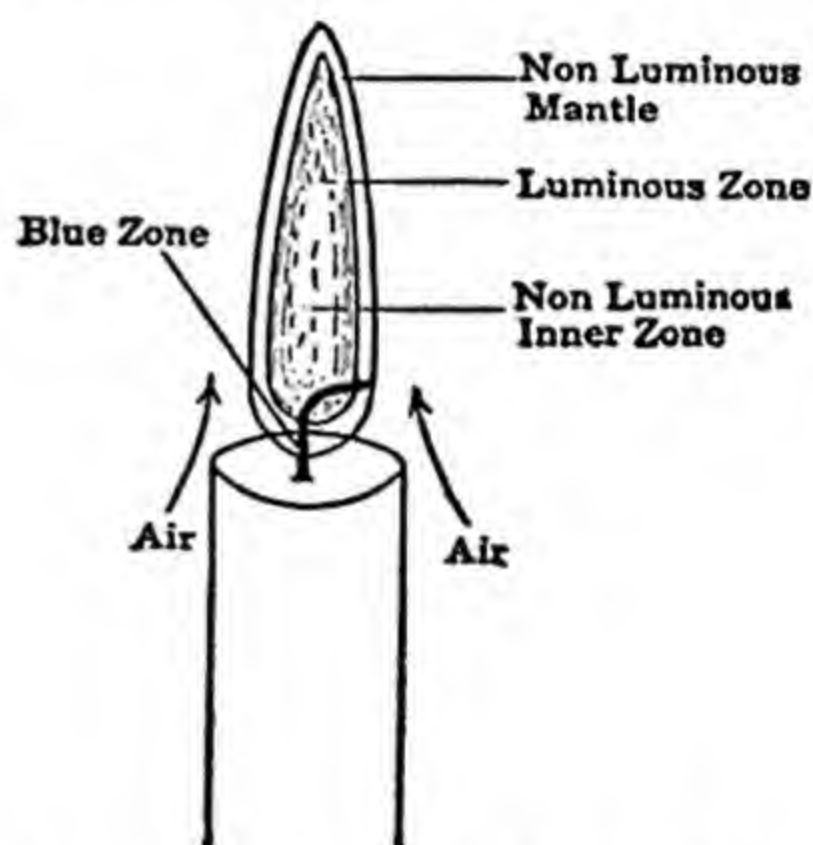


Fig. 165. Zones of a candle flame.

the same. It may be objected that solids also burn, but when flame is produced, as with wood or coal, it will be found that inflammable gases are distilling from the solid. Thus the flame of a candle is a gas flame. At the tip of the ordinary kerosene lamp-wick the heat of the flame vaporizes the liquid into gas. With hydrocarbons flames of at least three zones result. This is to be expected when we remember that hydrocarbons are "cracked" or decomposed by heat. There must be a zone of decomposition into ethylene, hydrogen, etc. This may be illustrated by using a Bunsen burner with air inlets open; the inner bluish-green cone, *A*, is sharply defined. With less air admitted, a luminous cone, *B*, envelops this, while surrounding the latter is a sheath of perfectly burned gases, *C*, almost invisible (Fig. 164).

Smithells made clear that in *A* there is some burning of the gas, as some carbon monoxide is present there, but cracking of the hydrocarbons into ethylene, acetylene, and hydrogen also occurs. In *B* (luminous cone) the carbon monoxide and hydrogen are burned, while the ethylene and acetylene are cracked into hydrogen plus carbon. It is largely due to the incandescence of this free carbon that the flame is luminous. A cold dish pressed into this zone becomes coated with carbon, since the carbon is cooled below its kindling temperature. The student will recall similar experiments with the flames of hydrogen sulfide, arsine, and stibine. (What were they?) Finally the hydrogen and carbon are completely burned in the outer sheath *C*.

There is a small cone of unburned gas at the tip of the burner and a match head may be held in this without ignition.

The hottest parts of a flame are just above the tip of *B* and about the middle of the outer sheath. Here the Bunsen flame reaches 1560° or 1570° . At the top of the burner the temperature is only 300° . When too much air is admitted to the base of the Bunsen burner the "ignition wave" sometimes travels downward faster than the gas flows upward. The result is that the flame *strikes back* and burns down in the Bunsen tube with an unpleasant odor and decided heating of the metal. The Meker burner prevents this by a heavy metal grid on top which cools any ignition wave so that the flame cannot run down the tube. Consequently much air may be admitted at the base and hotter flames obtained (as high as 1775°).

Safety Lamp. The principle of the Meker grid can be shown by thrusting a wire gauze halfway down on a flame. No flame appears above the gauze simply because the gas is cooled below its ignition temperature. Sir Humphry Davy in 1815 surrounded the coal miner's lamp with a heavy gauze and thus made it safe to carry such a lamp into coal mines containing fire damp (methane). Any methane diffusing through the gauze burns on the inside of the cage, but not on the outside, as the gauze chills the gas below its ignition point.

Flame arrestors of corrugated sheets of aluminum packed like a honeycomb are used today in the breathing tubes of oil tanks.

A plug of porous ceramic ware or of steel wool placed in a tube through which any inflammable gas is passing would also serve as a flame arrestor.

Exercises

1. What are the natural sources of hydrocarbons?
2. Why not use coal tar as a fuel?
3. If a gas containing some sulfur compounds were burned, would the products of combustion be unsafe in the house? Why?
4. Could a water-gas plant and a coal-gas plant cooperate to advantage?
5. If you cracked natural gas (CH_4) in the presence of steam, what products could you reasonably expect?
6. Toluene from coal tar would not supply war needs. Have we another adequate source?
7. What are the structural formulas of benzene, toluene, monochlor-benzene, phenol, aniline?
8. How is aniline prepared from benzene?
9. When benzene is ignited, the carbon is converted into carbon dioxide and the hydrogen into water. What weight of air would be required for the combustion of 250 g. of this hydrocarbon?
10. Why is phenol important? Toluene?
11. What is the liquefied gas sold for cooking in isolated homes?

References

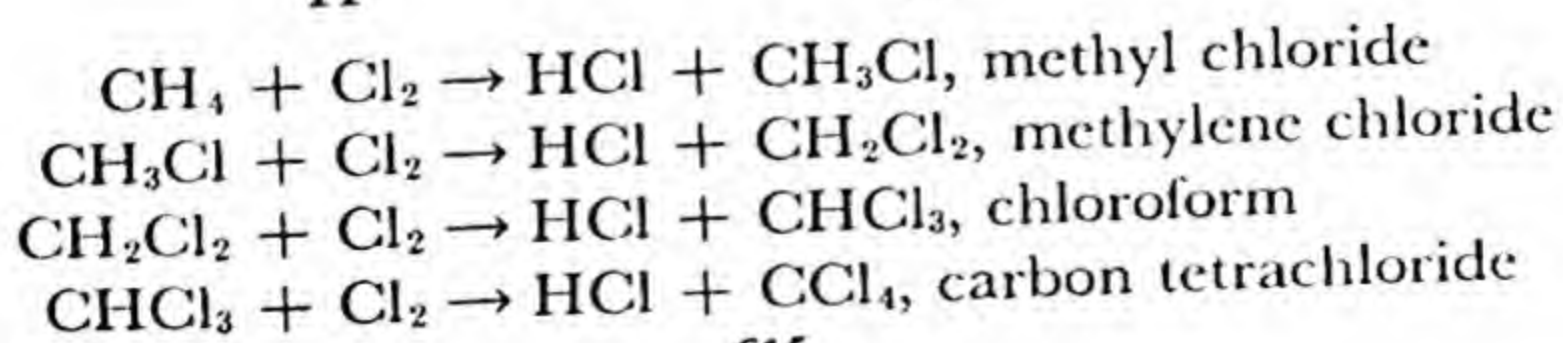
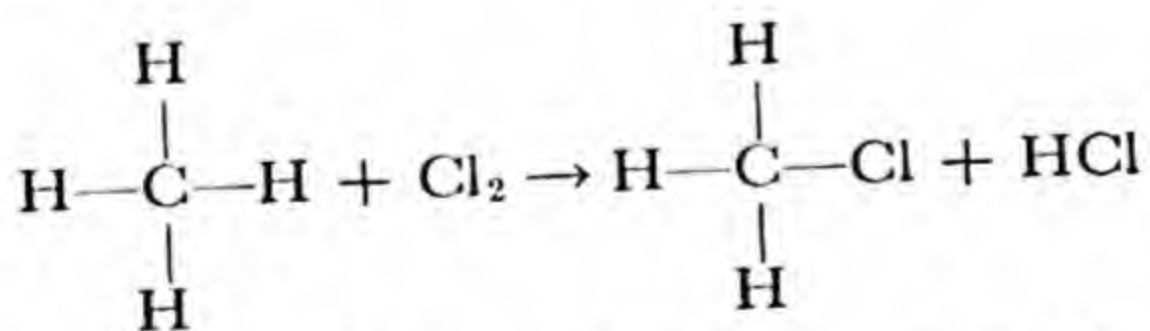
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Chapter 54 ALCOHOLS, ACIDS, FATS, AND SOAPS

There are probably 500,000 compounds of carbon, called "organic" compounds because prior to 1828 it was thought that they were organized or built up only in living animal or plant tissue. It was in 1828 that Wöhler synthesized urea, $\text{CO}(\text{NH}_2)_2$, and thus started an era of laboratory organic syntheses that has given the world countless useful substances never known in nature. It is a remarkable fact that carbon compounds constitute more than nine-tenths of all substances. We live in a carbon system and a water system but others are conceivable, if inferior.

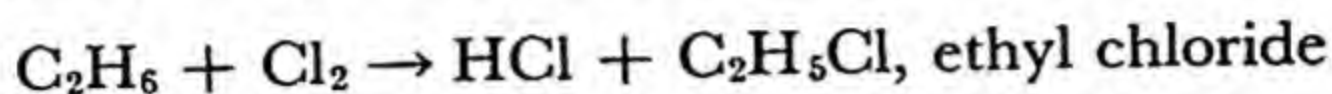
Organic chemistry is fundamental to biology, physiology, medicine, pharmacology, and agriculture, yet the sheer beauty of logical reasoning involved in its study would alone justify the development of the subject.

Derivatives of the Hydrocarbons. Methane slowly reacts with chlorine, first one atom of hydrogen being replaced by chlorine and, with longer treatment, all four hydrogen atoms being replaced:



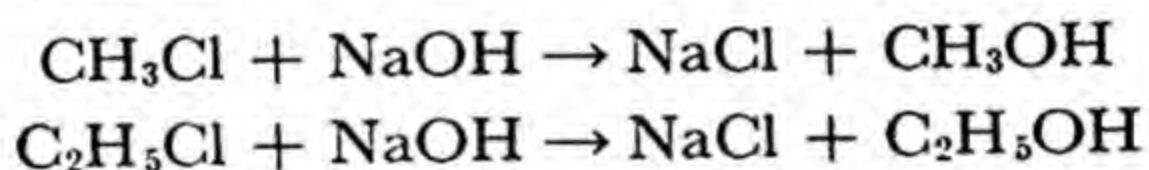
Chlorinated hydrocarbons such as carbon tetrachloride and trichlorethylene, are used in dry-cleaning and, during war, in degreasing tanks, guns, etc., shipped across the oceans.

Ethane reacts with chlorine in the same way:

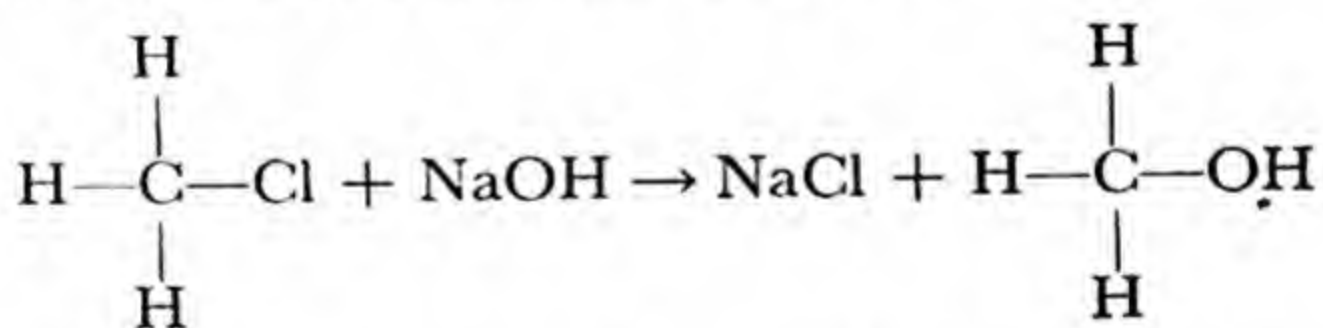


Chloroform and carbon tetrachloride are not made commercially by the above methods, but they may be so prepared. It will be noted that a new group is found in methyl chloride, the monovalent *methyl* group (CH_3). Also in ethyl chloride is found the monovalent *ethyl* group (C_2H_5). Methyl, ethyl, propyl, and similar radicals are called "alkyl" groups.

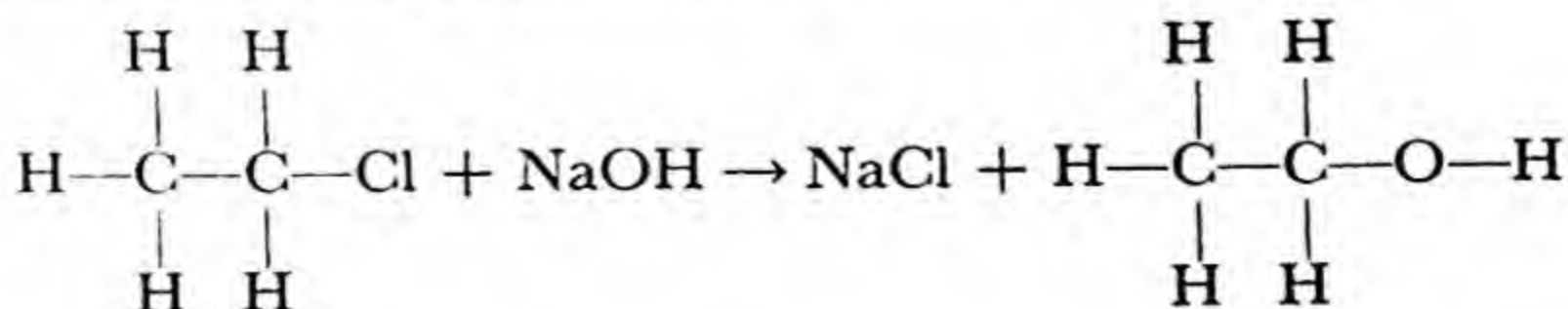
Starting with methyl chloride (which does not ionize as does sodium chloride), we can make *methyl alcohol* very simply (but not profitably). *Ethyl alcohol* can be formed in a similar manner:



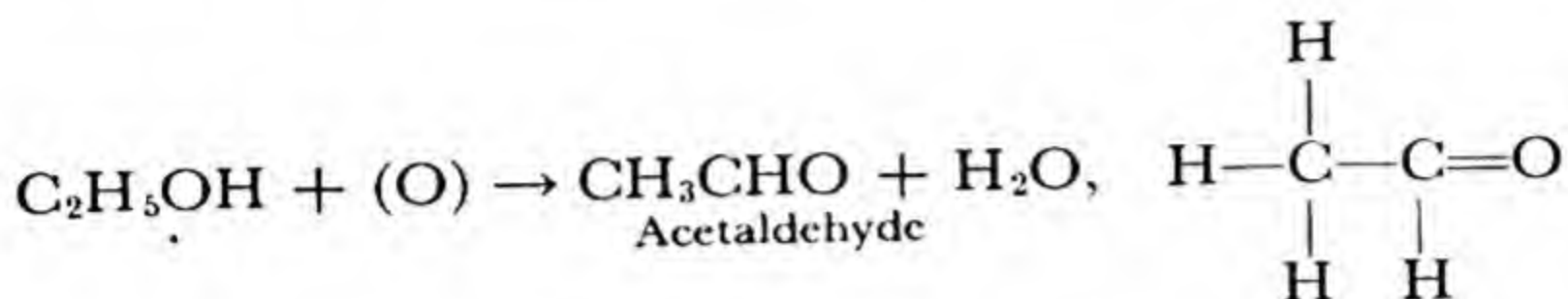
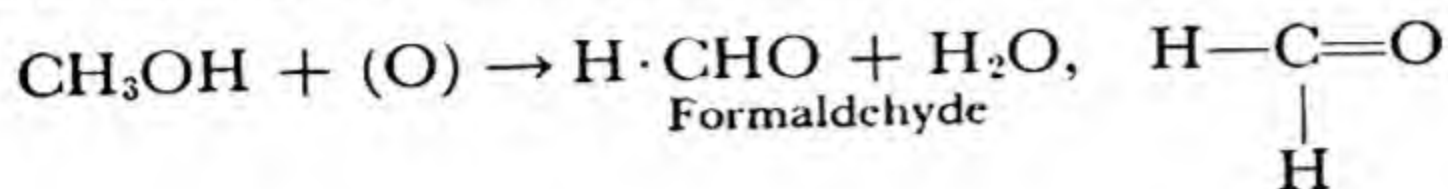
As it happens, there are better methods of preparing these important and famous (or infamous) alcohols, but this one is valuable in showing us the structure of alcohols:



Knowing the structure of methane to begin with, the structure given for methyl chloride follows, and hence we are positive that in methyl alcohol the hydroxyl radical must be attached directly to the same carbon atom that holds the other hydrogen atoms. By the same logic we are confident that the structural formulas given in the following equation are correct:

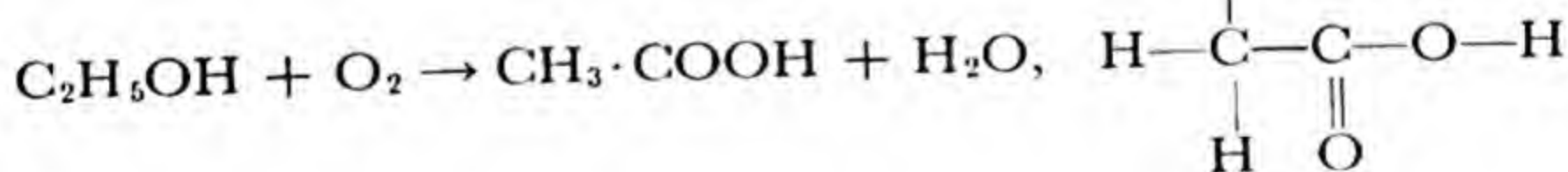
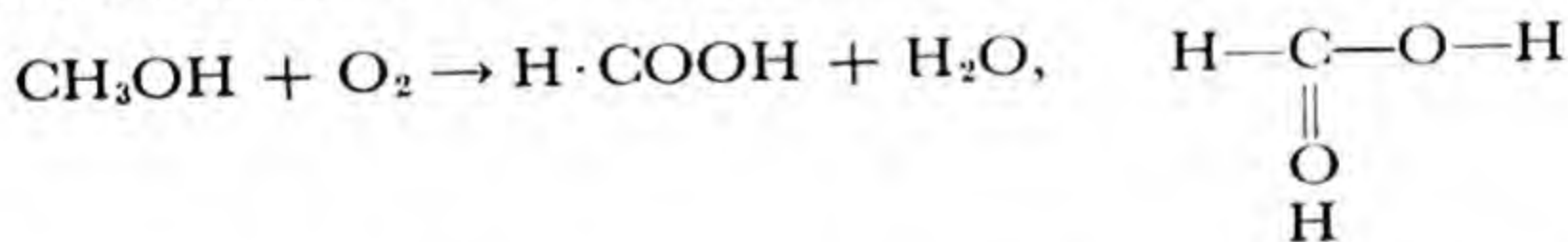


Having learned the general structure of alcohols, we can now proceed to show what will happen if we oxidize them (as with sodium dichromate and sulfuric acid):



Thus we see that two hydrogen atoms are removed from each molecule of an alcohol yielding as oxidation products, *aldehydes*, the first being formaldehyde, $\text{H} \cdot \text{CHO}$, and the second, acetaldehyde, $\text{CH}_3 \cdot \text{CHO}$. In each, and indeed in all aldehydes, the same group ($-\text{CHO}$) is found, so if "R" stands for any radical, CH_3- or C_2H_5- , etc., we might clearly represent any aldehyde as $\text{R} \cdot \text{CHO}$.

More vigorous oxidation of alcohols or of aldehydes produces another familiar class of compounds, the *organic acids*:



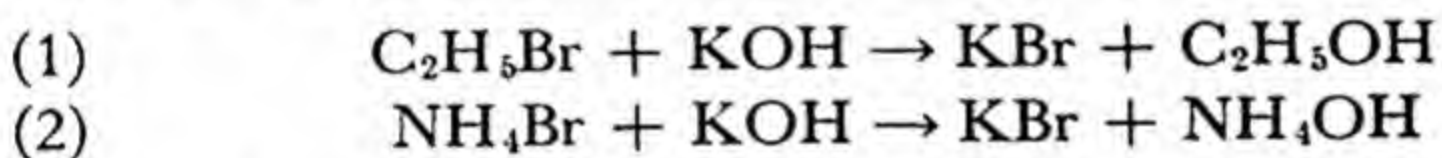
CHLORINE DERIVATIVES	ALCOHOLS	ALDEHYDES	ACIDS
Methyl chloride, CH_3Cl	Methyl alcohol, CH_3OH	Formaldehyde, $\text{H} \cdot \text{CHO}$	Formic acid, $\text{H} \cdot \text{COOH}$
Ethyl chloride, $\text{C}_2\text{H}_5\text{Cl}$	Ethyl alcohol, $\text{C}_2\text{H}_5\text{OH}$	Acetaldehyde, $\text{CH}_3 \cdot \text{CHO}$	Acetic acid, $\text{CH}_3 \cdot \text{COOH}$
Propyl chloride, $\text{C}_3\text{H}_7\text{Cl}$	Propyl alcohol, $\text{C}_3\text{H}_7\text{OH}$	Propionaldehyde, $\text{C}_2\text{H}_5 \cdot \text{CHO}$	Propionic acid, $\text{C}_2\text{H}_5\text{COOH}$
Butyl chloride, $\text{C}_4\text{H}_9\text{Cl}$	Butyl alcohol, $\text{C}_4\text{H}_9\text{OH}$	Butyraldehyde, $\text{C}_3\text{H}_7\text{CHO}$	Butyric acid, $\text{C}_3\text{H}_7 \cdot \text{COOH}$
$\text{R} \cdot \text{Cl}$	$\text{R} \cdot \text{OH}$	$\text{R} \cdot \text{CHO}$	$\text{R} \cdot \text{COOH}$

The first is formic acid, $\text{H} \cdot \text{COOH}$, and the second is acetic acid, $\text{CH}_3 \cdot \text{COOH}$. In nearly all organic acids we find the carboxyl group ($-\text{COOH}$). An important point to remember is that in these acids it is only the hydrogen atom in each carboxyl group that ionizes. The hydrogen atoms in the radicals never ionize. This is why the formula for acetic acid is frequently written as $\text{H} \cdot \text{C}_2\text{H}_3\text{O}_2$, setting apart the ionizable hydrogen. However, we prefer to use its halfway structural formula, $\text{CH}_3 \cdot \text{COOH}$.

Exercises

1. Start with propane and show, step by step, how to make an acid from it. Give the exact structure of each compound.
2. From what hydrocarbon could you make acetic acid? Give the steps.

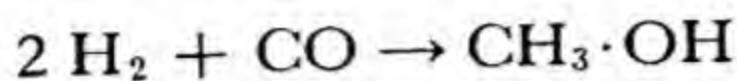
The Alcohols. The alcohols remind us of inorganic bases in their structure but not in their action:



There is a good deal of similarity between the above reactions, but there is this fundamental difference: reaction (2) is between ions, but ethyl bromide ($\text{C}_2\text{H}_5\text{Br}$) does not ionize, so it reacts as a molecule. When the products are examined it is found that the ethyl hydroxide or ethyl alcohol does not affect litmus paper, does not conduct electricity, and, in short, does not ionize at all. It appears, then, that a hydroxyl group attached directly to a hydrocarbon radical has very different properties (alcoholic) from a hydroxyl group attached directly to a metal (basic) or even to a non-metal (acidic). Any simple alcohol may be represented by the general formula $\text{R} \cdot \text{OH}$, where "R" is CH_3 , C_2H_5 , etc. Strange to relate, there are alcoholic groups in the sugars and in cellulose.

Methyl Alcohol (Methanol), CH_3OH . In commercial practice this alcohol has been made by the retort distillation of wood, hence its common name, "wood alcohol." The distillation of wood to yield charcoal parallels the distillation of coal to yield coke.

In 1924 there was developed a catalytic process for preparing methyl alcohol by the direct union of carbon monoxide and hydrogen under considerable pressure in the presence of zinc oxide and copper, or other catalysts:



A very pure product is prepared in commercial quantities at a cost lower than by wood distillation.

Methyl alcohol (CH_3OH), a colorless liquid boiling at 67.4° , is miscible with water in all proportions, is intoxicating, and extremely poisonous. It is much used as a solvent in varnishes, and as the starting point in the manufacture of formaldehyde.

In 1947, over 500,000,000 gallons of synthetic methanol were produced and only 2,500,000 gallons of crude methanol from wood. The price fell from \$1.10 to \$0.33 per gallon. The wood-distillation industry would cease to exist were it not for wood charcoal, necessary in the manufacture of a certain quality of steel.

Ethyl Alcohol (Ethanol), C_2H_5OH . Ethyl alcohol which is commonly known as "grain alcohol," is a colorless, inflammable liquid boiling at 78° and miscible with water in all proportions. It is not poisonous, although when taken to excess in strong beverages the effect on the system is distinctly injurious. Like fire, alcohol is a good servant, but a bad master. As a servant it is one of the best solvents in the laboratory and the starting point in the manufacture of many useful compounds. Internal-combustion motors can use it, with

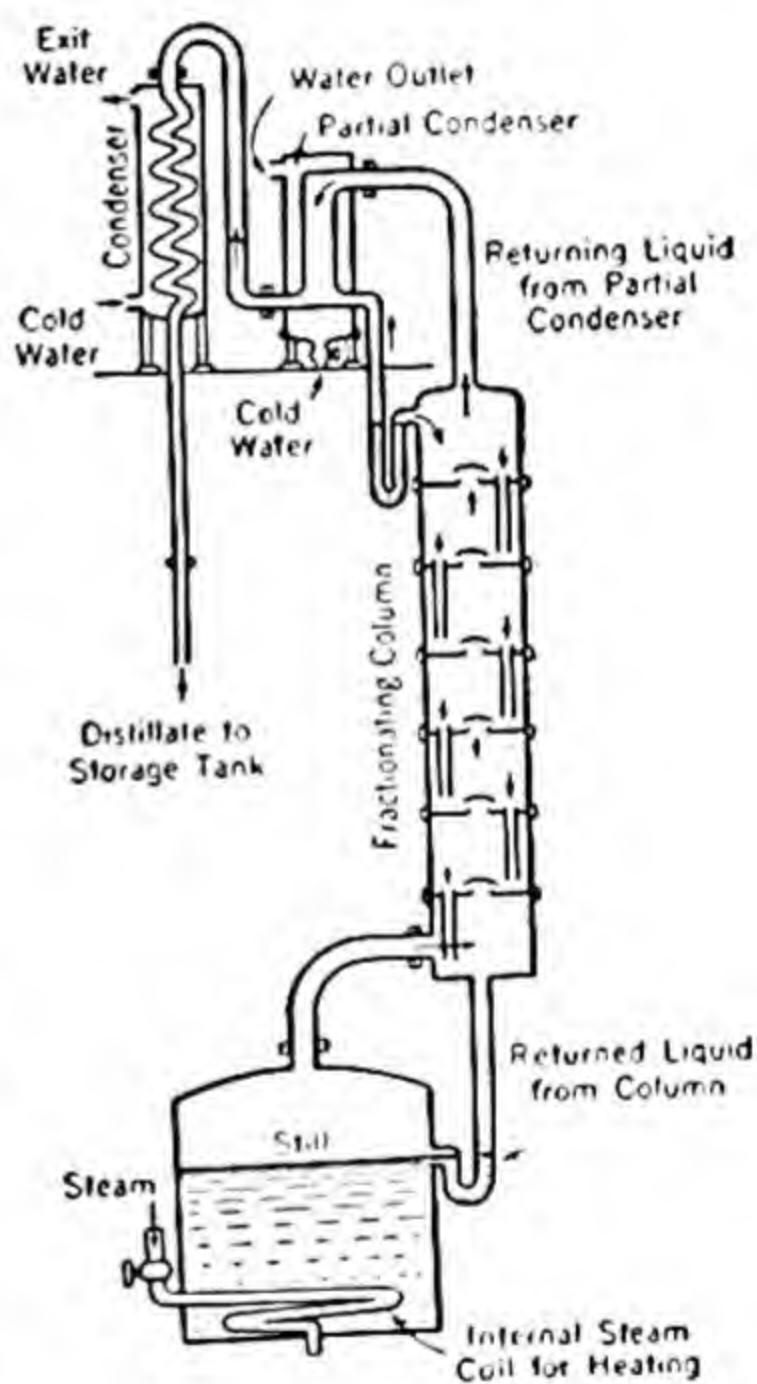


Fig. 166. Column still. The more readily condensed water vapors return to the still while the more volatile alcohol vapors reach the condenser.

certain adjustments, and when our coal and oil deposits are exhausted the world will probably turn to cheap alcohol as a power fuel. It can be made from the starch and cellulose and sugars of plants, hence the sun's heat and power can be utilized in this way.

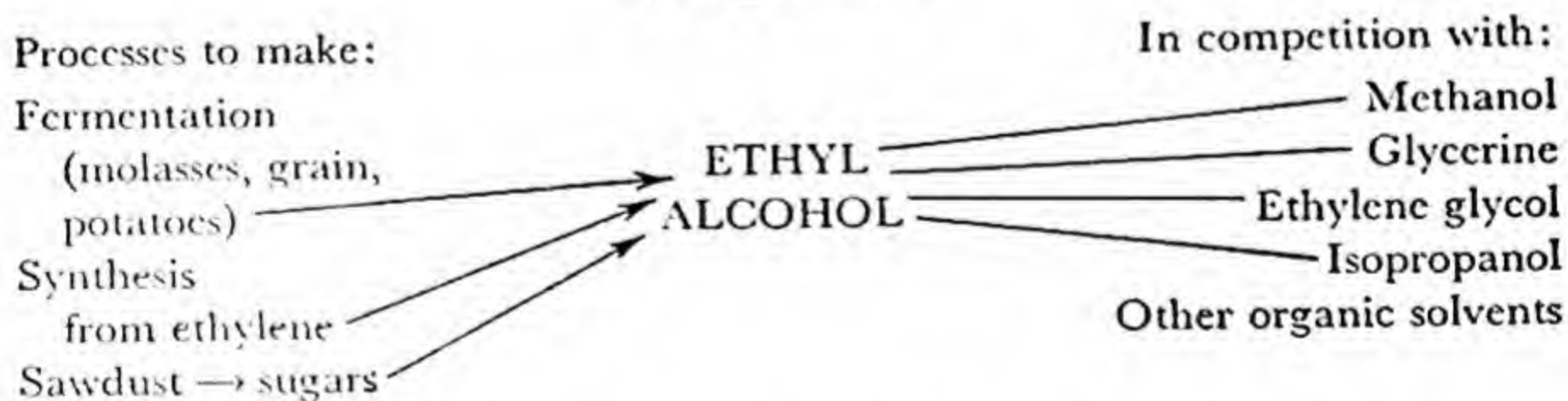
Alcoholic fermentation of sugars supplies us with a great part of the ethyl alcohol used. Glucose is the only common fermentable sugar, so cane sugar, malt sugar, starch, and cellulose must all be converted into glucose before they can yield alcohol. The reactions involved are given later. The column-still concentrates the 10 per cent alcohol content of fermented "mash" to 95 per cent industrial alcohol.

The capacity of plants making alcohol from ethylene (from petroleum refineries) is 100,000,000 gallons. In the past we produced 200,000,000 gallons yearly from grains and molasses, but war needs (synthetic rubber, explosives, etc.) called for 600,000,000 gallons in 1944. Production is now back to normal.

The Fischer-Tropsch catalytic process of making liquid fuels from natural gas may yield a great amount of alcohol as a by-product.

The manufacture of the smokeless powder for a single 12-inch shell requires a barrel of alcohol, much of which is recovered.

Competition



Absolute alcohol, when listed for taxation by our government, is termed "200° proof" and the ordinary 95 per cent alcohol 190° proof. The standard is 100° proof or 50 per cent alcohol by volume.

In some countries it was desired that alcohol should be added to gasoline, but the ordinary 95 per cent alcohol of commerce does not mix with gasoline, so absolute alcohol must be prepared

at some additional cost. Removal of the last 5 per cent of water by distilling over quicklime is too expensive.

The problem was solved in France by distilling the 95 per cent alcohol in the presence of water-insoluble liquids (such as the benzene from coal tar). Benzene, water, and alcohol form a ternary mixture (of 74.1 per cent, 7.4 per cent, and 18.5 per cent) boiling at 64.9°C . Benzene and alcohol form a binary mixture (of 67.6 per cent and 32.4 per cent) boiling at 68.2°C . Using an efficient fractionating column the ternary mixture comes off first, carrying *all* the water with it; then comes the binary mixture, carrying the remainder of the benzene; and absolute alcohol is left behind. By regulating the supply of alcohol and benzene the process is made continuous. Such constant-boiling mixtures are "azeotropic." Methylene dichloride can be used in place of the benzene.

This useful method of *azeotropic distillation* is now applied to the dehydration of acetic acid and other separations of mixed liquids where similar principles hold.

Other Alcohols. *Glycerine* (glycerol, to be exact) is an alcohol, although we are inclined to forget that fact, since it is non-intoxicating. Its structure shows the presence of alcoholic hydroxyl groups, three of them in each molecule. Glycerol is a color-

less, syrupy liquid of sweetish taste. Since it is hygroscopic it remains moist and is often put in mixtures because of this property. It is also a leather softener. A great deal is used in tobacco, in some medicinal preparations, in making nitroglycerine, synthetic resins, cosmetics, and for hydraulic mechanisms of autos

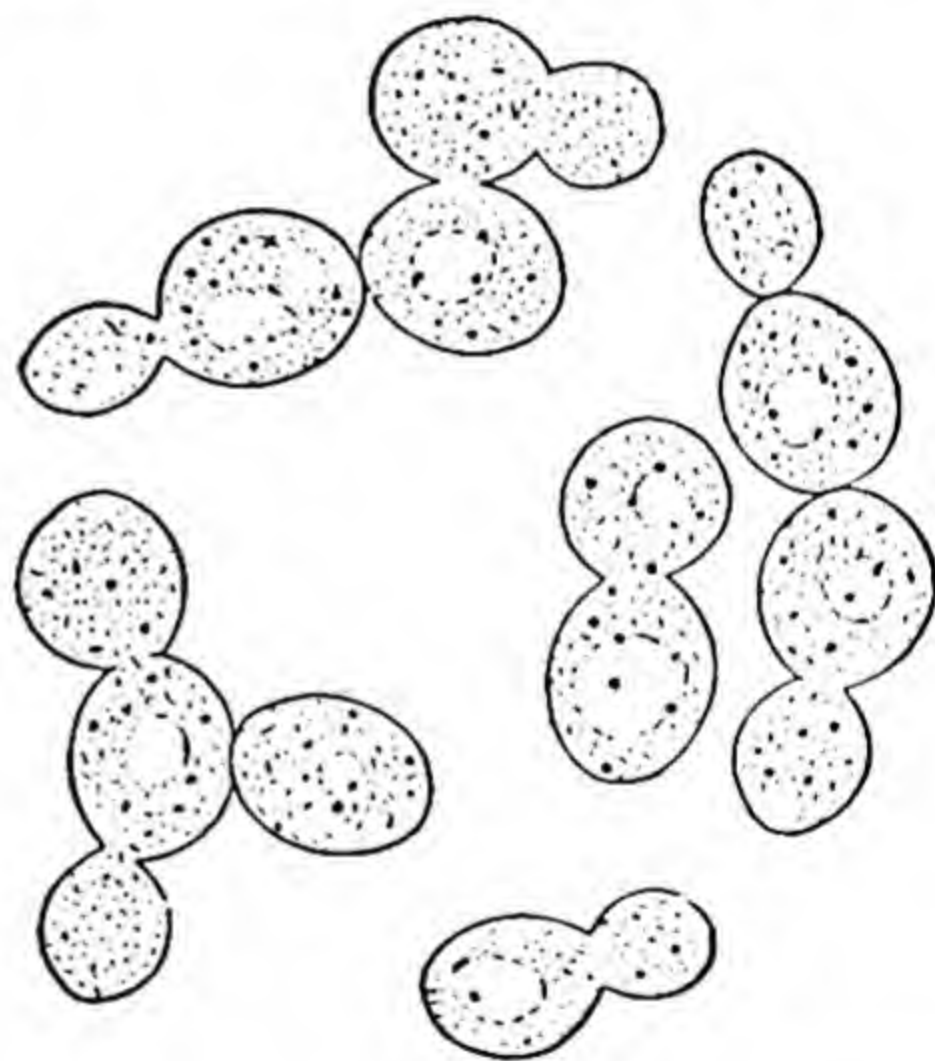
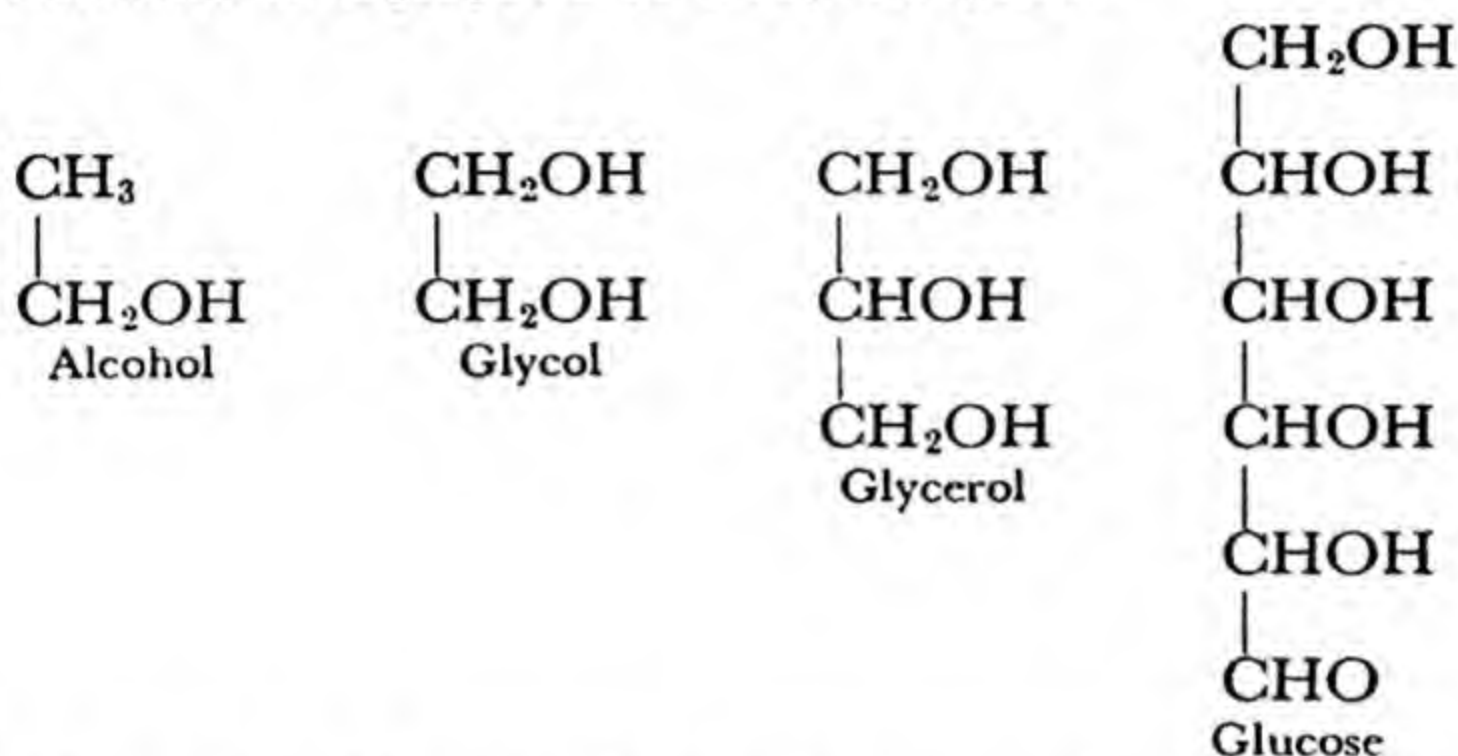


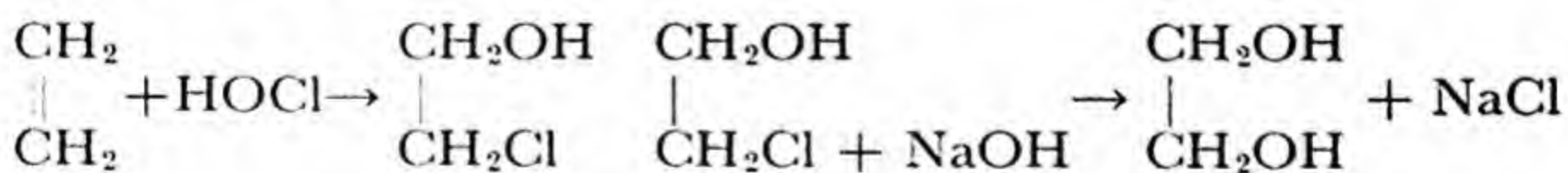
Fig. 167. Yeast cells multiply with enormous rapidity by budding. They quit working when they ferment a liquor to 15 per cent alcohol.

and guns. Both glycerol and glycol are much used in anti-freeze solutions for autos. When fats are broken down in the soap making process, glycerol is a by-product. It is now possible to make great quantities of glycerol from certain products of the petroleum refinery. Over 170,000,000 lbs. were produced in a recent year.

The alcoholic hydroxyl group also is found in the sugars. A comparison of structural formulas of ethyl alcohol, glycerol, and a typical sugar such as glucose is interesting. Ethyl alcohol may be represented as C_2H_5OH or $CH_3 \cdot CH_2OH$.



Ethylene Glycol, very similar in properties and structure to glycerol, is now made in large quantities by cracking natural gas to ethylene, treating the ethylene with hypochlorous acid, and hydrolyzing to glycol:



This glycol is produced to the extent of 300,000,000 lbs. yearly, mainly for anti-freeze purposes.

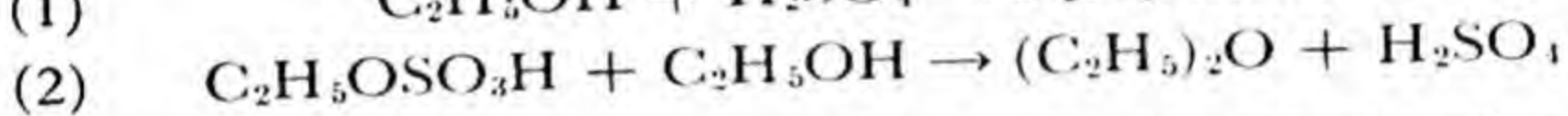
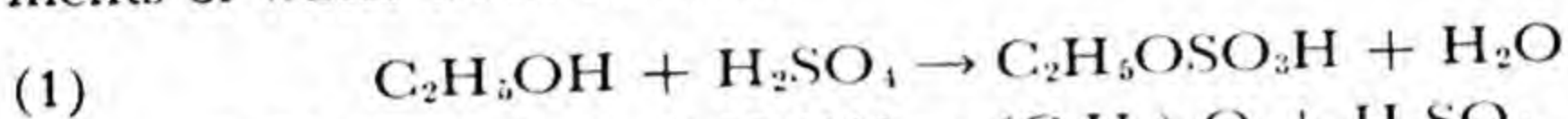
The monoethyl ether of glycol ("cellosolve") is widely used as a solvent in lacquers. Glycol dinitrate is used to the extent of millions of pounds to lower the freezing point of the nitroglycerine in dynamite (thawing out has caused explosions). Nitroglycerine freezes at $+13^\circ C$. while glycol dinitrate freezes at $-23^\circ C$. Propylene glycol, sprayed as a fine mist into air, removes bacteria.

Isopropyl Alcohol, C_3H_7OH . The isopropylene of oil-refinery gases is treated with sulfuric acid and the sulfated product hydrolyzed to make this useful alcohol. Over 110,000,000 gallons were produced in a recent year.

It closely resembles ethyl alcohol in solvent power and in physical properties. Distillation after brief digestion with sodium hydroxide secures the anhydrous alcohol, boiling at 82.4° . Produced in large quantity at a low price, it offers competition for ethanol but not as a beverage. It has a bad taste.

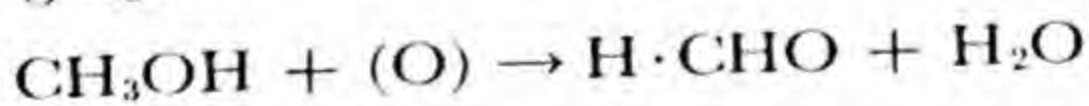
Similar alcohols with a higher carbon content can be prepared by catalyzed reaction of ethylene, C_2H_4 , or other olefins, with water gas.

Ethers. The ether we know as an anaesthetic is produced by the action of hot concentrated sulfuric acid to remove the elements of water from alcohol.



This diethyl ether $(C_2H_5)_2O$, is a colorless liquid of very low boiling point, 35° , very inflammable, and only slightly soluble in water. It is a useful solvent for a great number of substances. Dimethyl ether is $(CH_3)_2O$ and any ether could be represented as R_2O .

Aldehydes. Wood alcohol can be oxidized moderately enough to fall short of becoming formic acid and thus formaldehyde may be secured. Other aldehydes are made in similar fashion. They are all reducing agents.



In practice the vapors of methyl alcohol, mixed with air, are passed through a tube containing heated copper gauze as the catalyst.

The general formula for all aldehydes may be written $R \cdot CHO$, in which R represents any radical such as methyl (CH_3) or ethyl (C_2H_5).

Formaldehyde is used as a 40 per cent aqueous solution called formalin. It is a valuable germicide and antiseptic. A large

amount is used to react with phenol (carbolic acid) in the preparation of "*bakelite*." Over 400,000,000 pounds are used every year, more than half of it for bakelite and such plastics.

Acetone, $(\text{CH}_3)_2\text{CO}$. This colorless liquid is used as a safe solvent for compressed acetylene and in the manufacture of chloroform. It is a solvent for many substances, such as fats and varnish materials, and is of very great importance as a solvent in the manufacture of cordite and some smokeless powders. Over 380,000,000 pounds were required in one war year.

By the synthetic process acetylene is catalytically converted into acetaldehyde, this into acetic acid, and the acid into acetone by catalytic decomposition. Acetone is also made commercially by the fermentation of cornstarch through the action of a very useful bacterium (*Clostridium acetobutylicum*). Probably most of our acetone is now made by the catalytic dehydrogenation of isopropyl alcohol but some is made from propylene.

Acetone is merely the simplest member of a series of *ketones*

whose general formula is

$$\begin{array}{c} \text{R} \\ \diagdown \\ \text{C}=\text{O} \\ \diagup \\ \text{R} \end{array}$$

Acids. There are different series of organic acids, but the "fatty-acid" series is the one of most common interest. The fats contain glycerine compounds of some of these acids of higher molecular weight, hence the name. All the members of this series are monobasic. Most of them are liquids, but such acids as palmitic and stearic are solids. Formic and acetic acids are the simplest members and the general formula may be written $\text{R} \cdot \text{COOH}$.

Formic Acid, $\text{H} \cdot \text{COOH}$. Formic acid, $\text{H} \cdot \text{COOH}$, is found in stinging nettles and red ants, adding zest to the sting or bite. It may be made by sufficient oxidation of methyl alcohol, but there is little demand for the acid.

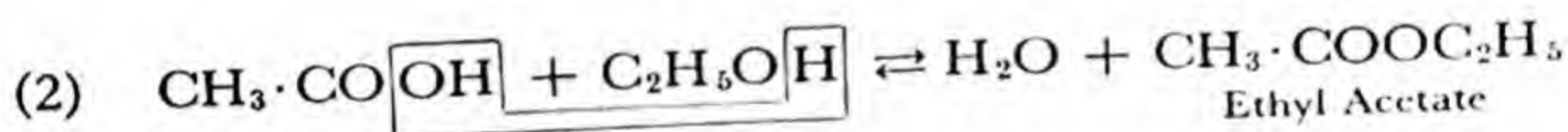
Acetic Acid, $\text{CH}_3 \cdot \text{COOH}$. Acetic acid, when anhydrous, is a colorless liquid (*glacial acetic acid*) freezing to a crystalline solid at 18° . With water it forms a colorless solution. The odor is sharp and penetrating.

The anhydride of acetic acid $(\text{CH}_3\text{CO})_2\text{O}$, is essential to the manufacture of cellulose acetate silk, the best type of rayon.

This country uses 360,000,000 pounds of acetic acid yearly; some of it is a product of wood distillation but most of it is prepared from acetylene by catalytic methods. Much of it is converted into acetic anhydride for the manufacture of cellulose acetate.

Vinegar may be made from "hard" cider in a week or two if the *mother of vinegar*, which aids the oxygen of the air in uniting with the alcohol, is spread through a barrel of beechwood shavings (tasteless wood). Perforations in the barrel admit the necessary air and as the cider trickles through again and again, excellent contact is made. Ordinary vinegars contain four or five per cent acetic acid.

Esters. Alcohols react with organic acids to form water and esters. These esters remind us somewhat of salts in their method of formation (but not in properties) and hence are often called *etheral salts*. A comparison of the reactions producing inorganic salts and etheral salts helps to clarify the relations:



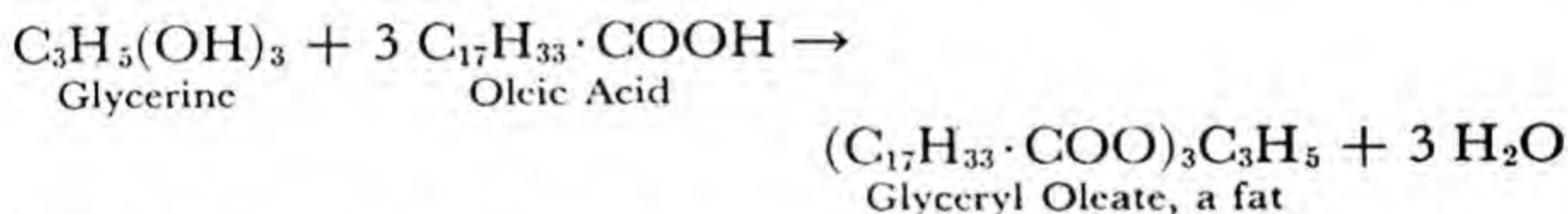
Reaction (1) is the neutralization of an acid by a base. A hydrogen ion from the acid unites with the hydroxyl ion from the base to form water. But reaction (2) is not neutralization, since the alcohol does not yield hydroxyl ions. All we can say is that in effect the *hydroxyl group* of the acid unites with the hydroxyl *hydrogen* of the alcohol to form water and that the hydrocarbon radical (C_2H_5) of the alcohol replaces the acid hydrogen of the acid, forming an etheral salt, in this case ethyl acetate. In general esters may be represented by $\text{R} \cdot \text{COOR}'$, where R and R' are any hydrocarbon radicals. Inorganic acids also react with alcohols and the products are usually called esters also. Ethyl nitrate ($\text{C}_2\text{H}_5 \cdot \text{NO}_3$) is the ethyl ester of nitric acid and is dangerous to prepare. The so-called nitroglycerine is really glyceryl trinitrate, an ester of nitric acid and the alcohol glycerine.

Most fruit flavors and odors are due to the presence of esters.

- How could you make methyl propionate? Propyl butyrate?
- Here is a chart comparison of typical organic compounds. Name each member.

HYDRO-CARBONS	HALOGEN DERIVATIVES	ALCOHOLS	ALDEHYDES	ACIDS	ETHYL ESTERS
CH ₄	CH ₃ ·Cl	CH ₃ OH	H·CHO	H·COOH	H·COOC ₂ H ₅
C ₂ H ₆	C ₂ H ₅ ·Cl	C ₂ H ₅ OH	CH ₃ ·CHO	CH ₃ ·COOH	CH ₃ ·COOC ₂ H ₅
C ₃ H ₈	C ₃ H ₇ ·Cl	C ₃ H ₇ OH	C ₂ H ₅ ·CHO	C ₂ H ₅ ·COOH	C ₂ H ₅ ·COOC ₂ H ₅
etc.	etc.	etc.	etc.	etc.	etc.

Fats. The esters derived from glycerine (as the alcohol) and the higher fatty acids, such as palmitic and stearic (and oleic from a related series), are called fats. This means that fats are a particular kind of ester. We do not have to synthesize the fats — plants and animals have done that for us, but if desired it could be done:



There are very few simple fats in animal and plant tissue. Olive oil is largely glyceryl oleate ("olein") but lard is a mixture of 40 per cent glyceryl palmitate (palmitin) and stearate (stearin) with 60 per cent olein. Beef suet contains the same fats but is harder because it contains only 25 per cent olein. Olive oil and cottonseed oil are liquids because they contain fully 75 per cent olein. Butter is a mixture of several fats. When it becomes rancid with age some of the esters are decomposed, yielding free acid, and the offensive odor of butyric acid makes itself known.

Oleomargarine is a butter substitute in great demand. To make it, beef fat, from which much stearin has been removed by crystallization at 24°, is stirred with some oil to soften it and churned with milk to give it the butter flavor. When the mixture is chilled, the "oleo" separates. Vegetable fats are worked into "oleo" to make the "nut margarines," and vitamin A is added to much of it. We used 650,000,000 pounds of oleomargarine in a

recent year, and exported 150,000,000. Of all kinds of fats the world uses 26,000,000 tons.

Edible liquid fats are in great demand as salad oils and cooking oils. Olive oil is the most expensive, but enormous quantities of purified cottonseed oil, peanut oil, corn oil, and some sunflower seed oil have found a ready market. The United States often produces over one billion pounds of cottonseed oil in a year, yet all this was formerly wasted when cottonseed was thrown away.

In this country we normally use nearly twelve billion pounds of fats annually, of which soybean oil constitutes an important portion. We import huge quantities of vegetable fats.

Soybean oil is really edible but it has been used mostly in the paint and varnish industry. Production in 1947 was 1,500,000,000 pounds.

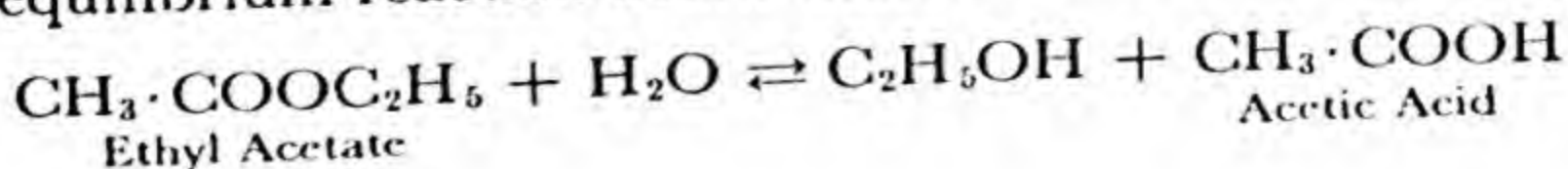
Whale oil, partly hydrogenated to remove odor, has had considerable demand among the poorer classes of Europe as a food. One large blue whale may yield 25 tons.

Drying Oils. Linseed oil (from flaxseed) has long been the chief liquid "vehicle" for paint pigments. It is oxidized (not dried) in the air to yield a tough film. We produce half of our needs, the remainder coming from Argentina. Soybean oil, up to 20 per cent, is mixed with it without loss of quality, in fact treated soybean oil with quick-drying properties may replace linseed oil.

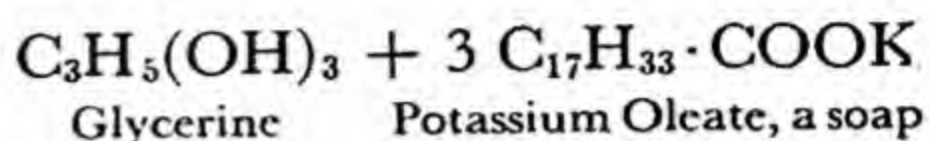
Tung oil, from the tung nuts of China, is more rapidly oxidized than linseed oil and hence has special uses in varnishes and lithograph inks. Tung trees in great number are now growing on our Gulf Coast.

Castor oil, a special engine lubricant, becomes a good drying oil when catalytically dehydrated. Castor oil retains its viscosity when diluted with gasoline, so has wide use as an engine lubricant. **Perilla oil** and a few others are also drying oils.

Soaps. Esters are hydrolyzed by water, especially by hot water. The equilibrium reaction below indicates this:



This hydrolysis takes place faster if a base is present. Of course a salt of the fatty acid must be formed when a base is used.



This reaction is called saponification of the ester, and the salt of the fatty acid is called a soap.

When a fat is saponified by hot water in the presence of a suitable catalyst, glycerine and the free acid are the products.

For soap-making coconut oil is almost an essential. Especially true is this of quick-lathering soaps. Now it is possible to prepare fatty acids of the coconut oil type by controlled oxidation of certain petroleum hydrocarbons.

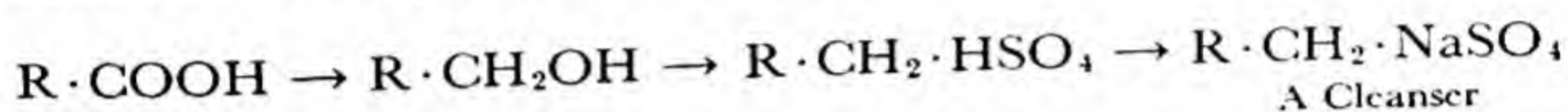
Soap-making on a commercial scale is usually a matter of boiling cheap mixed fats with caustic soda if the firm, "hard" soaps are desired, or with caustic potash if "soft" soaps are wanted. The soft soap of early pioneer days was made by using the lye (K_2CO_3) leached from wood ashes, and such lard and tallow as accumulated about the house. Greater refinements are demanded now. Soap is "salted out" by common salt, is partly dried and pressed into cakes. The remaining solution is distilled for its glycerine, the important by-product.

By a new process fats are heated with water under 500 pounds pressure, yielding pure glycerine and the fatty acids. To make a soap from these acids is simply a matter of neutralization with a base. Pure glycerine is readily recovered.

Aluminum stearate (insoluble in water) is a soap but not a cleanser. Yet it has considerable use in water-proofing textiles, as a suspending agent and flattening agent in paints, and in wax polishes. Heavy metal soaps are not cleansers.

If civilization is measured by the amount of soap used, it must be significant that the United States makes and uses 2,800,000,000 pounds annually.

Soapless detergents are now in competition with soaps. Long-chain fatty acids, such as those from coconut oils, are hydrogenated under high pressure and at elevated temperatures with a catalyst present. The —COOH group is reduced to the $\text{—CH}_2\text{OH}$ group or, in other words, the acid becomes an alcohol. This alcohol is next sulfated (with sulfuric acid) and neutralized to yield sodium salts. There are many useful types of synthetic detergents. Such products form a cleansing froth in hard water and in sea water and are useful also in aiding the uniform penetration of dye solutions in cotton and other fabrics. Some, unlike soap, can be used in acid solution.



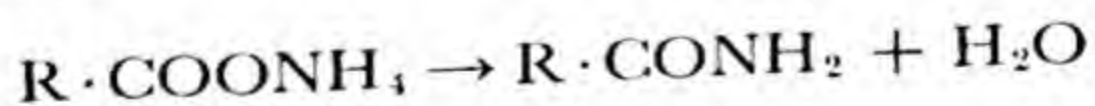
Production of synthetic detergents and other surface-active material has risen to 700,000,000 pounds yearly. Much of this production derives from petroleum.

White household soaps contain 30 per cent water but soap chips contain only 8 to 12 per cent.

Shaving cream contains an acid soap, the product obtained by half neutralizing the fatty acids with potassium hydroxide or some organic base.

Over 100,000,000 pounds of soap were used in 1944 in preparing an emulsion of the materials to be polymerized into synthetic rubber.

Derivatives of the Fatty Acids. It is possible to make such derivatives of the fatty acids as alcohols, aldehydes, amines, ketones, etc., some of them very promising in application to plastics and synthetic rubbers. The amides, readily made merely by heating ammonium soaps, are solids suitable for the water-proofing of fabrics:



In normal years there are available huge quantities of fats from which fatty acids may be freed.

Review Drill

		Name these
C_2H_6	Ethane	C_6H_6
C_2H_5Cl	Ethyl chloride	C_2H_5Cl
C_2H_5OH	Ethyl alcohol	C_6H_5OH
$C_2H_5NH_2$	Ethyl amine	$C_6H_5NO_2$
$C_2H_5NO_2$	Nitroethane	$C_6H_5NH_2$
$(C_2H_5)_2O$	Diethyl ether	$C_6H_5 \cdot CHO$
$(C_2H_5)_2CO$	Diethyl ketone	$C_6H_5 \cdot COOH$
$C_2H_5 \cdot CHO$	An aldehyde	—
$C_2H_5 \cdot COOH$	An acid (propionic)	$C_6H_5 \cdot CH_3$
$C_2H_5 \cdot COOR$	An ester	$C_6H_5(NO_2)_3 \cdot CH_3$
$C_3H_5(C_{17}H_{33} \cdot COO)_3$	A fat (glyceryl oleate)	—
$C_{17}H_{33} \cdot COONa$	A soap (sodium oleate)	$C_3H_5(OH)_3$

Exercises

- How many grams of glucose must be used to prepare 690 g. of alcohol, assuming the yield to be 90 per cent? What will be the volume of CO_2 evolved (standard conditions)? (See page 636.)
- How many grams of the soap, potassium oleate, can be made from 415 grams of glyceryl oleate, $C_3H_5(C_{17}H_{33} \cdot COO)_3$?
- Compare the costs of alcohol from corn at 50 cents a bushel and molasses at 5 cents per gallon.

1 bu. corn yields 2.5 gals. alcohol

1 gal. molasses yields 0.4 gal. alcohol

- What can you make from ethane, C_2H_6 (and how)? Give the structure of ethane and of a few of these derivatives. Some may be made in one step, some in several step reactions.
- What are the rival sources of common alcohol?
- Write and prove the structure of ethyl alcohol.
- What soap substitutes are available?
- Why are fats vital to a nation?
- What are three possible sources of glycerol?
- If 10 per cent of alcohol should be added to gasoline for motor fuel, why would it be impossible to use the ordinary 95 per cent ethyl alcohol? Absolute, or 100 per cent, alcohol is required.
- Why is acetone in such great demand?

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Chapter 55 THE CARBOHYDRATES

A most important class of compounds, including starch, the sugars, and cellulose, contains carbon and just twice as many hydrogen atoms as oxygen atoms in each molecule. This means that the two latter elements are found in the proportion to form water, hence the name, carbohydrates. On heating, some of these give off water formed in the general decomposition but it is not held like water in hydrates. Plants take carbon dioxide from the air and water from the soil, and build them into the cellulose of wood, cotton, linen, grasses, etc., or the starch of potatoes, arrow-root, cassava, rice, and the other roots and grains. Molecules of both starch and cellulose are probably large, represented by some multiple of $C_6H_{10}O_5$.

Cellulose. Cellulose is more fully discussed on page 643 but it may be stated here that this carbohydrate makes up half the weight of dry wood. Pure linen and cotton fibers, and filter paper, as well as the stringy parts of many vegetables and grasses represent cellulose.

Starch. Starch is stored in roots like potatoes, in grains, and in the trunk of the sago palm. Rice contains 75 per cent starch, corn 50 per cent, and potatoes 20 per cent. It is a white substance of very high molecular weight $(C_6H_{10}O_5)_x$, insoluble in cold water but swelling in hot water to a pasty translucent mass. When heated sufficiently it forms a yellowish, sweet substance called dextrin. The crust of bread (baked at a higher temperature than the moist interior) probably owes its sweetness to dextrin. Dextrin

is used as a mucilage on envelopes and postage stamps. Starch itself in the form of a paste is commonly used in hanging wall paper, also as sizing in the textile industry. It is a valuable food when cooked, but is far less digestible raw. Having alcoholic hydroxyl groups it can, of course, be nitrated. Nitro-starch is a very safe explosive and is used to the extent of thousands of tons in filling hand grenades. In the laundry, starch is indispensable. It is also one of the chief sources of ethyl alcohol. When treated with water and a trace of acid as a catalyst it is hydrolyzed into glucose.

In 1940 we imported 352,000,000 pounds of tapioca starch, mainly for use as an adhesive. A waxy maize, developed in Iowa from Chinese popcorn, yields a perfect substitute for this tapioca adhesive.

Starch ethers are possibly going to compete with cellophane, rayon and other cellulose products.

The Sugars. There are two important classes of soluble sugars, monosaccharides and disaccharides. The distinction is easy. Sugars of the formula $C_{12}H_{22}O_{11}$ can be broken down into simple sugars, usually of the formula $C_6H_{12}O_6$. Such simple sugars cannot be resolved into still simpler sugars.

Complex sugars (Disaccharides) $C_{12}H_{22}O_{11}$	{ Sucrose (cane sugar) Maltose (malt sugar) Lactose (milk sugar)
Simple sugars (Monosaccharides) $C_6H_{12}O_6$	{ Dextrose (glucose) or grape sugar Laevulose (fructose) or fruit sugar Galactose Mannose

The sugars contain alcoholic hydroxyl radicals or groups and, since there are several sugars of the formula $C_6H_{12}O_6$, there must be several different arrangements of the groups. Some of the rarer sugars are decomposed only by definite strains of bacteria and so are used in the recognition of these bacteria.

Sweetness is not the infallible test for "sugars." For that matter some sugars are bitter. Saccharin is 500 times as sweet and perillaldehyde (alpha-antialdoxime) is 2000 times as sweet as sucrose, yet they do not have the structure of sugars, therefore are

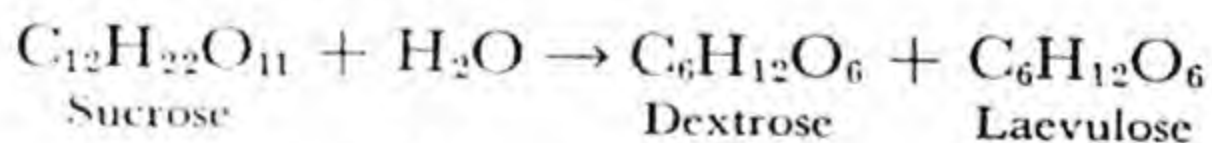
not sugars. Some "sugars," on the other hand, are not sweet. If sucrose is rated in a scale of sweetness as 100, laevulose is 173, glucose (dextrose) 74, maltose 32, and lactose (milk sugar) 16.

Sucrose, $C_{12}H_{22}O_{11}$. Cane sugar, beet sugar, and maple sugar are all the same when purified. In Europe most sucrose comes from beets.

Sugar from cane is produced in Cuba, Hawaii, Java, Brazil, and Louisiana — most of it in Cuba. The cane is crushed to extract the juice, which is then treated with lime to coagulate impurities that would otherwise ferment. The clarified juice (12–18 per cent sugar) is boiled down in vacuum pans at as low a temperature as 50°C . because if boiled at atmospheric pressure and above 100° the sugar would be decomposed. Concentrations of 65 per cent are possible. When the sugar crystallizes it is whirled free from molasses in centrifugals and shipped to refineries for further purification.

This country produces more than 1,000,000 tons of sugar yearly from sugar beets but we eat 7,000,000 tons. The world wants 35,000,000 tons. By careful breeding the sugar content of beets has been increased to over 15 per cent.

Sucrose treated with acid as a catalyst reacts with water to form "invert sugar," a mixture of dextrose and laevulose. Curiously enough, this mixture, with some delicious impurities, makes up the main part of honey:

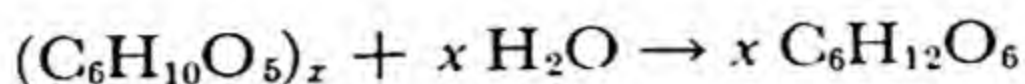


During the first World War Germany, in need of nitroglycerine, converted thousands of tons of sugar into glycerine by the aid of yeasts in a special environment.

Knowledge of cane sugar and its delights was first brought to Europe from India in 327 B.C. by Alexander the Great. It was Columbus who carried sugar cane on to the New World.

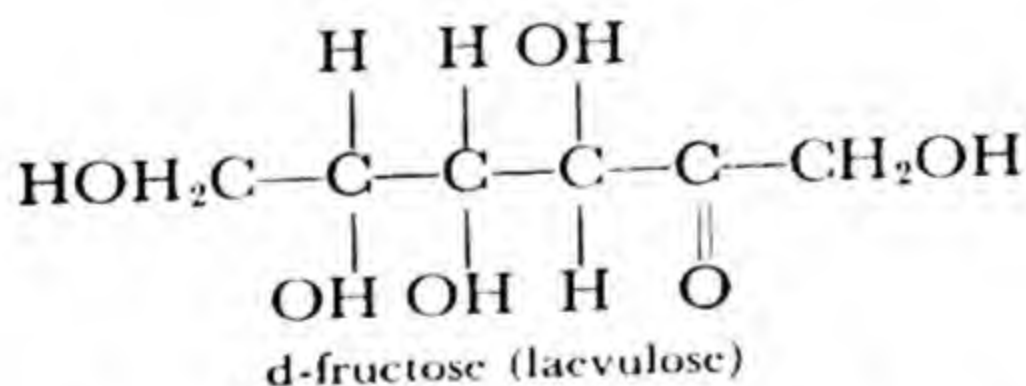
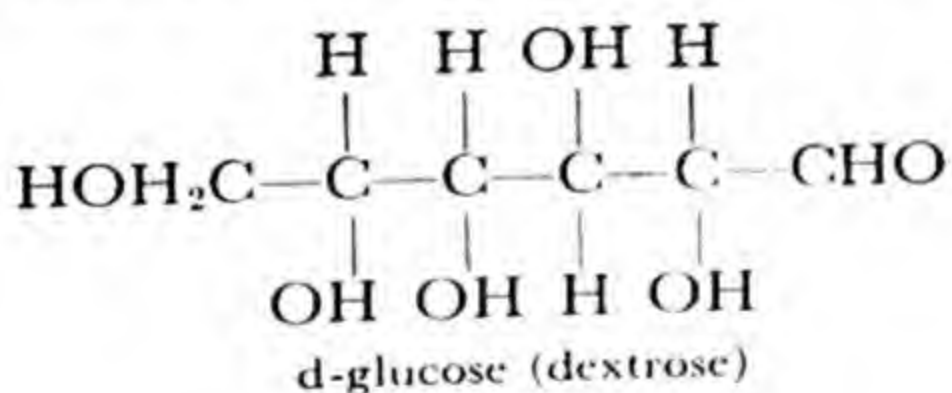
Glucose, $C_6H_{12}O_6$. This is also called dextrose and even grape sugar, since it occurs in grapes and raisins. It is less sweet than sucrose, but is a good food; in fact it is partly digested cane sugar. Both starch and sucrose, all the complex sugars in fact, are con-

verted into glucose by the digestive fluids. Glucose is made commercially from starch which is heated with water and some acid as a catalyst:



Hydrochloric acid is used in a 0.1 per cent solution. The trace of sodium chloride formed on neutralization with sodium hydroxide does no harm. Glucose has 32 isomeric forms. Glucose is used in candies, soda fountain syrups, baked goods, and even as a filler for cheap soaps and leather. As an intermediate compound in the manufacture of alcohol (as well as whisky and beer) from the starch of cereals, glucose is of vast importance.

Laevulose and Inulin. When inulin, a carbohydrate closely resembling starch, is hydrolyzed in similar manner laevulose (fructose) is formed instead of dextrose (glucose). The root tubers of the Jerusalem artichoke are rich in inulin. One variety has been found capable of yielding two tons of laevulose per acre. Glucose and laevulose are isomers but they differ structurally in that one is an aldehyde sugar and the other a ketone sugar:



Enzymes and Fermentation. The yeast plant, a very lowly but useful organism made up of microscopic cells, secretes two chemicals known as invertase (or sucrase) and zymase. These are true catalysts. Enzymes differ from the inorganic catalysts in that they are compounds secreted by living organisms. Sucrase splits sugar (in the presence of water) into glucose and fructose, both

fermentable, although fructose is less so than the glucose. Zymase finishes the work begun by the sucrase and converts the simple sugars into alcohol and carbon dioxide:



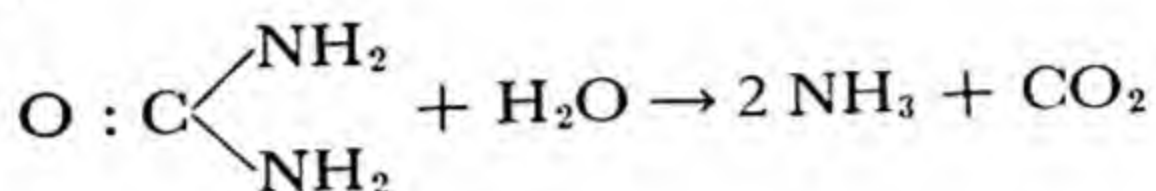
It is an interesting fact that a germinating seed (barley, for example) develops enzymes as it sprouts. These catalysts, amylase and maltase, convert the insoluble starch of the seed into soluble glucose capable of being carried by the sap of the growing plant. The brewer borrows this clever device from the sprouting grain in order to make alcoholic drinks from starchy cereals. He allows barley to sprout — of course amylase and maltase are developed in the process — then heats the sprouts to kill all life. The catalysts, mere chemicals, are uninjured. This “malt” is then mixed with the warm, moist, crushed grain and the starch is hydrolyzed to maltose, malt sugar, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$. Yeast is then added and the malt sugar further hydrolyzed to form glucose. The zymase completes the change by fermenting this glucose into alcohol. By distillation a 45 per cent alcoholic solution well known as “whisky” is secured. Beer is simply the fermented liquor made from barley without distillation. Wine is fermented from grape juice by the wild yeast found on the skins of the grape. Even in as common a process as bread-making the yeast causes a fermentation with release of carbon dioxide and consequent “rising” of the dough.

Starch (by amylase) \rightarrow maltose
Maltose (by maltase) \rightarrow glucose
Glucose (by zymase) \rightarrow alcohol

There are many other enzymes than those secreted by yeast or by sprouting grains. The animal body secretes enzymes which manage digestion of food. Pepsin is familiar to all of us. Molds also develop organic enzymes. As a rule they cause putrefaction. Bacteria contain enzymes. There are six kinds of enzymes in a ripe banana and fourteen in certain molds. The study of molds, yeasts, and bacteria from the enzyme viewpoint is rapidly becoming a matter of commercial importance in the production of organic compounds.

Many, perhaps all, enzymes are activated by specific inorganic ions. Pepsin works at its best in 0.2 per cent acid (HCl of the stomach) and amylase of the pancreatic juice needs traces of chlorides and phosphates. Such activating ions are called co-enzymes.

Enzymes act upon astonishing amounts of material. Sucrase converts 200,000 times its own weight of sucrose. Urease, an enzyme of the globulin class, hydrolyzes urea so fast at 20° C. that it (urease) produces 120 times its own weight of ammonia every five minutes:



Amylase can transform 4,000,000 times its own weight of starch.

Amylase, converting starch to sugar, has use in desizing textiles; proteases, changing more complex protein molecules into simpler ones, serve in removal of gum from raw silk and of hair from hides; and pectinase, attacking pectin materials, clarifies fruit juices.

Some enzymes are proteins and a very few have been crystallized, but others seem to consist of a colloidal protein "carrier" joined to some simple active group.

Bacteria as Chemists. Bacteria are the simplest forms of plants with such marvelous ability to multiply by cell-division that a single cell of some species can form more than 16,000,000 similar organisms in twenty-four hours. Each bacterium is a mass of colloidal protoplasmic material surrounded by a thin semipermeable wall. So small are they (some of them beyond the power of the microscope to see) that their surfaces, relative to mass, are enormous, and consequently the speed with which they manufacture toxins or harmless products, as the case may be, is appalling. Without the glass lenses of the compound microscope we would know little about bacteria.

Dangerous though many species of bacteria are, yet many others are essential to higher animal and plant life. In the ruminant animals (cattle, etc.) intestinal bacteria attack cellulose but bacteria in the human intestine cannot do this.

Chemists are now studying the chemistry of bacteria themselves with promising results. Not only may we learn more about immunity from disease, but we may compel bacteria to run large chemical factories for us. Of course we

have always allowed the nitrifying bacteria on the roots of clover, alfalfa, and other legumes to convert the free nitrogen of the air into invaluable plant food: nitrites, nitrates, and ammonia.

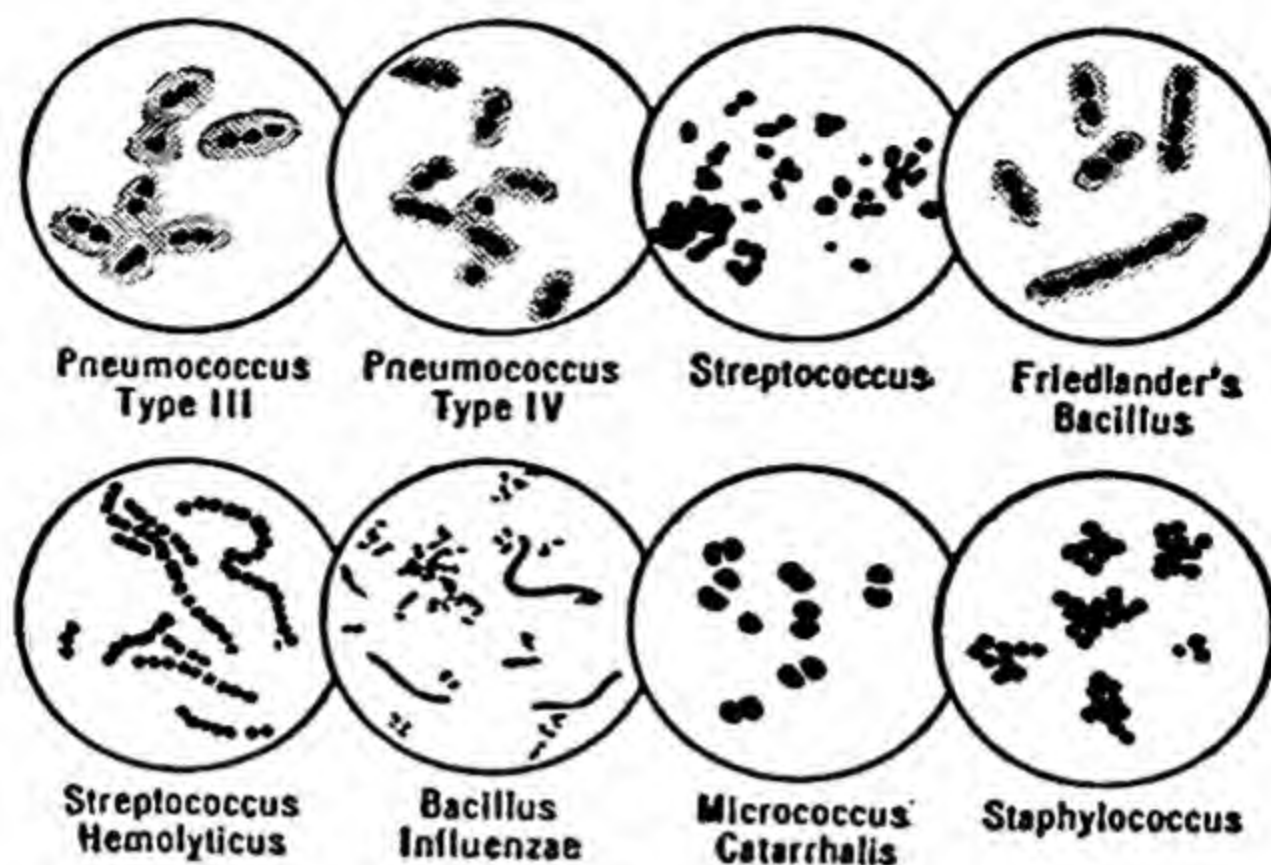


Fig. 168. Bacteria as chemists.

Butyl alcohol is now being produced on a large scale (for the cellulose lacquer industry) by the friendly coöperation of *Clostridium acetobutylicum* which converts starch into butanol, acetone, ethanol, hydrogen, and other products.

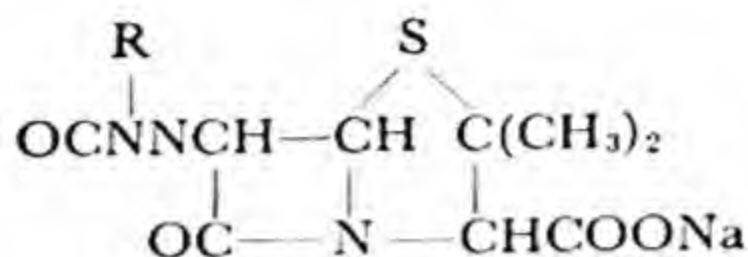
Molds as Chemists. The molds, of which there are thousands of species, are more complex than bacteria and yeasts. A large number of chemical



products may be manufactured by molds, e.g., penicillin and citric acid. The species, *Aspergillus niger*, acting on molasses, etc., produces millions of pounds of citric acid yearly. Molds produce enzymes of industrial value.

Penicillin, a recent and invaluable drug, is secreted by the mold, *penicillium notatum*. Its great success has led to the discovery of streptomycin and other antibiotics in various molds. A new field in chemistry and medicine has been opened. The chemist with a knowledge of bacteria and molds has a splendid opportunity.

Pencillin has been isolated in four or five variations and its basic structure determined.



Exercises

1. By what steps could you change starch into acetic acid? Could you change cellulose into acetone?
2. Ten grams of a carbohydrate give, on complete combustion in air, 15.43 g. of carbon dioxide and 5.79 g. of water. What is its formula?
3. What weight of dextrose would be required to prepare 432 g. of alcohol containing 95 per cent of $\text{C}_2\text{H}_5\text{OH}$ by weight? Add 5 per cent to your result because the efficiency of conversion is only 95 per cent.
4. How many milligrams of invert sugar are present in each milliliter of a solution prepared by inverting 15 g. of sucrose, and diluting the solution to one liter?
5. What are the products of the hydrolysis of (a) starch, (b) sucrose, (c) inulin? Compare the physical and chemical properties of starch and glucose. Could you name eight useful fermentations in the food industry (some of them ancient) caused by molds, yeasts, or bacteria?
6. What powerful medicine is made by a mold?
7. In the preparation of beet sugar certain salts must be removed from the juice. Could exchange resins be used, as in water purification? How?

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Chapter 56 CELLULOSE AND ITS ESTERS. DYEING. PLASTICS

Paper. Wood, in general, is made up of long fibers of cellulose $(C_6H_{10}O_5)_x$ cemented together by a gummy substance called lignin. In paper making this lignin is dissolved by digesting chips of the wood with a solution of chemical reagents. The pulp of cellulose fibers is then shaken on a sieve through which the water drains, and the fibers are matted in a sort of "warp and woof" system. It is this interlacing of fibers that gives paper its strength. After passing through rolls to squeeze out the remaining water, the paper sheet is coated with a rosin size or glue size which serves to prevent undue spreading of ink. Usually the wet pulp is bleached and often dyed. Glazed papers, that crack on creasing, are loaded with clay, which gives body to the paper. The best writing paper may be made from linen rags.

One giant machine making coarse but strong "kraft" paper ran steadily for two years delivering a sheet nineteen feet wide at a rate of one mile in 4.5 minutes.

The principal chemical processes used today are the sulfite, soda, and sulfate.

The Sulfite Process involves cooking wood chips with calcium bisulfite solution under pressure. The Soda Process utilizes a cooking with sodium hydroxide to produce book paper, and is mainly used for hardwoods, spruce, fir, and hemlock.

The Sulfate Process is wrongly named for it employs a mixture of sodium sulfide and sodium hydroxide in the cooking operation;

it is used with pine wood, to make coarse wrapping paper (kraft) and fiber container board.

The Chlorine Process, developed in Italy, begins with the digestion of wood, straw, or grasses in dilute sodium hydroxide and continues with use of chlorine gas as a delignifying agent. A weak alkaline wash and a hypochlorite bleach complete the treatment. The process is rapid and requires no pressure.



Fig. 169. Hand-made paper would be woefully inadequate for the printed pages of today. (Courtesy Bjarne Johnson.)

In a single year the United States made 1,256,000 tons of unbleached kraft paper for brown bags, wrappers, etc.

In the effort to maintain continuous wood-pulp production in the United States McKee has developed a hybrid poplar that grows as large in 8 years as do ordinary poplars in 45 years. Herty has made successfully white paper suitable for newspaper stock from the slash pine of the South. The pine is cut when about 8 or 12 years old, before rosin develops.

The importance and size of the paper industry are evident from the fact that in the United States 24,000,000 tons of paper (220 pounds per person) are made annually, one-third of it for fiber board. It is no wonder that machines have to make paper, rolling along from wet pulp to finished product, 17 feet wide, at a speed of 1200 feet per minute.

Most papers are made from spruce, fir, hemlock, pine, and softwoods in general.

Over 700,000 tons of straw are used annually in this country to make corrugated strawboard for boxes. Cheap sodium silicate adhesive adds greatly to the box strength. Celotex insulation is made from "bagasse," waste cellulose fiber of sugar cane.

Cellulose. The cellulose molecule $(C_6H_{10}O_5)_x$, has been shown by the X-ray to consist of 100–200 glucose units in long chains. Fifty such chains make up a bundle or micelle.

Cotton is nearly pure cellulose. The stringy part of vegetables is cellulose, but man makes little progress in digesting such fibers.

The by-products of the cotton seed, once a nuisance, are worth \$250,000,000 annually in this country alone. These products are oil, meal (for stock food), and linters (short fibers). Our usual cotton crop is 12,000,000 bales of 500 pounds each.



Fig. 170. Cotton boll.

Cellulose deserves a great deal of attention because it is the world's greatest crop. When petroleum, natural gas, and coal and some minerals are exhausted we shall make liquid fuels and substitutes for metals from this crop. Already we make houses, clothing, and books from it; we change it chemically into alcohol, stock food, movie film, high explosives, substitutes for paint, and other useful products. Intensive chemical research has worked miracles with coal and petroleum;

now it is time to attack cellulose with all our power. A plant is now in operation making alcohol from sawdust by acid hydrolysis to yield sugars which are then fermented.

Recently an absorbable gauze for surgeons' use has been prepared by oxidizing the —OH groups in cellulose to —COOH groups by the aid of nitrogen dioxide.

Cellulose Nitrates. When cellulose is attacked by concentrated nitric acid the hydroxyl groups of the cellulose unite with hydrogen of the acid to form water. At the same time a cellulose nitrate is formed. Concentrated sulfuric acid must be present to take up the water set free in the reaction.

In cellulose nitrate (an ester) of the non-explosive type (pyroxylin) only the two —OH groups represented on the outside of the ring in Fig. 171 are nitrated. In cellulose acetate (an ester) only the two outer —OH groups are acetylated — an acetyl group, $\text{CH}_3\cdot\text{CO—}$, replacing the hydrogen atom of each —OH . In ethyl cellulose (an ether) a $\text{C}_2\text{H}_5\text{—}$ group replaces a hydrogen in each of the two outer —OH groups.

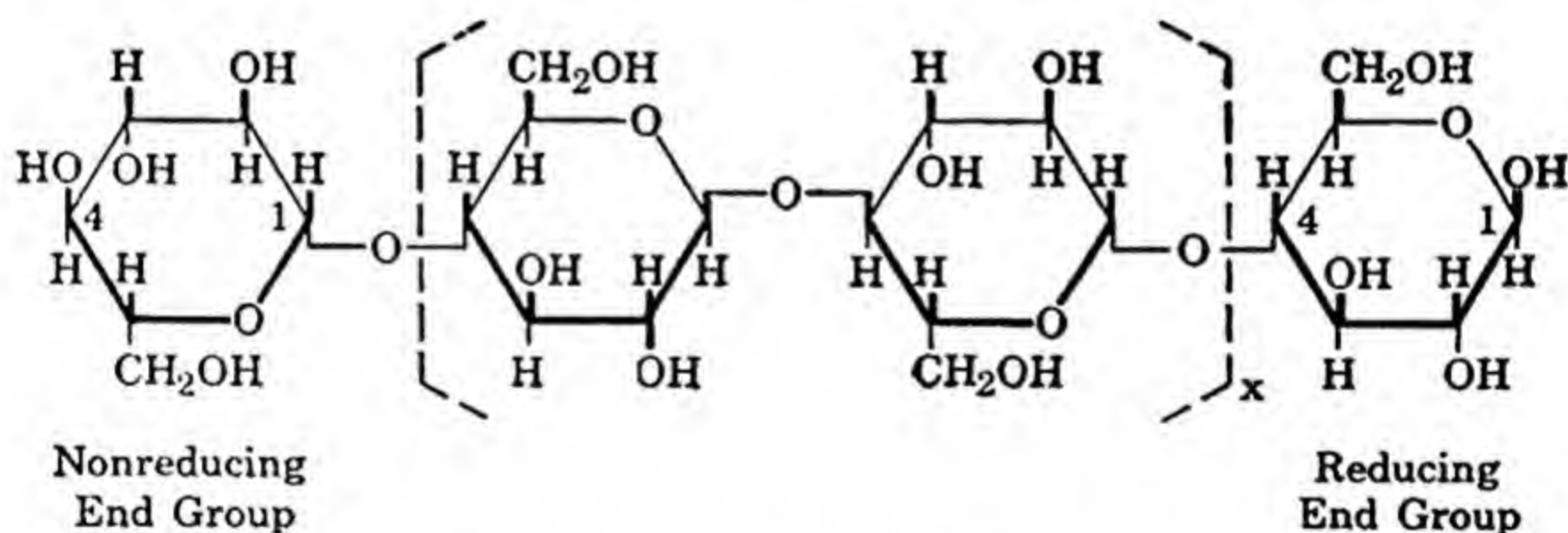


Fig. 171. A unit of the large cellulose molecule, showing different positions of hydroxyl groups of different reactivities.

Draw the structural formulas of these extremely useful commercial products: cellulose nitrate, cellulose acetate, and ethyl cellulose.

Explosives. With vigorous nitration by concentrated nitric and sulfuric acid a high explosive results, but with less vigorous nitration the non-explosive pyroxylin (about 12 per cent nitrogen) or "soluble cotton" is formed. Guncotton (about 13 per cent

nitrogen) burns harmlessly, but is exploded by a detonating cap. When it is dissolved in ether-alcohol and some vaseline is added, a "gel" is obtained that dries to a tough horny mass, called smokeless powder. In practice the pasty mass is forced through dies so that the dried solid is perforated by small holes. On burning in the gun the surface increases so that the force of explosion is not all exerted in one shattering instant but gathers strength as it progresses. In modern warfare all guns are fired with smokeless powder. The British cordite is a mixture made of guncotton, nitroglycerine and petroleum jelly dissolved in acetone. On evaporation of the acetone cordite results.

Nitroglycerine dissolves certain types of nitro-cotton to form a jelly (gelatin dynamite) much used in mining. With addition of ammonium nitrate the "ammonia dynamite" suitable for rock blasting is prepared. Common *dynamite* is usually a mixture of nitroglycerine, wood meal, and sodium nitrate. Ethylene glycol dinitrate is added to lower the freezing point of the nitroglycerine to the safety limit.

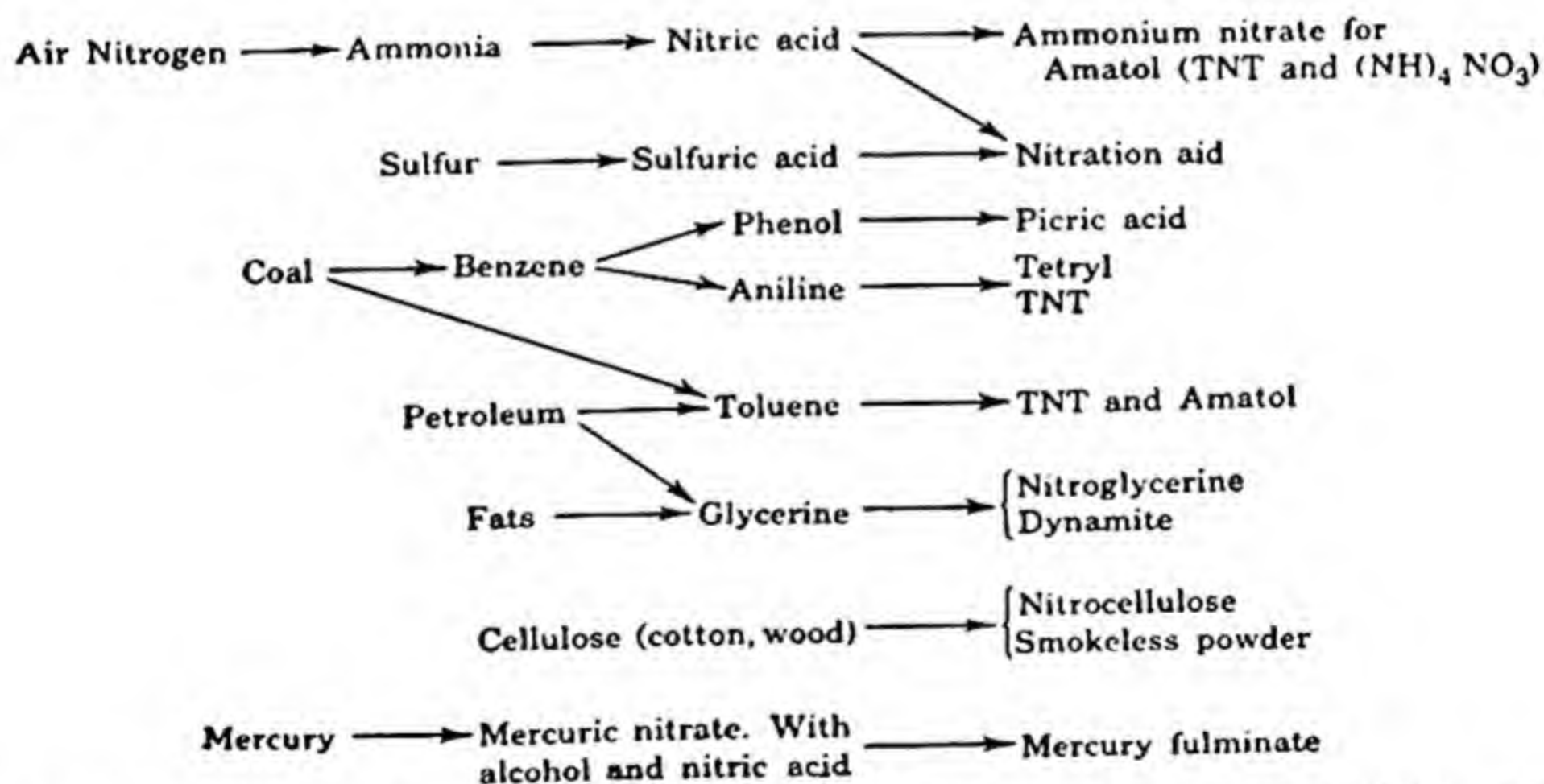


Fig. 172. Source of explosives. Nitric acid is used in making every explosive on the right, above. "Amatol" is a mixture of TNT and ammonium nitrate. Tetryl (tetranitroaniline) is the booster charge in shells, is more sensitive than TNT. Mercury fulminate, the detonating charge, is sixty times as sensitive as TNT. Lead azide is similar in sensitivity to mercury fulminate. "RDX" and "PETN" are among the most recently developed powerful explosives. RDX, much used in bombs and, in plastic form, for localized demolition, is derived from ammonia and formaldehyde. It is usually mixed with TNT. The atomic bomb is in a class by itself.

It is not to be thought that such manufacture is merely a deadly art. Without powerful explosives in great quantities there would be fewer railroad tunnels, no Panama Canal, less coal mined, less of most minerals secured, and no loosening of the hardpan where fruit trees are to be planted.

More than 30,000 men slaved eleven years to dig a three-mile tunnel for a Roman aqueduct. Thanks mainly to explosives the same tunnel could be built today by 100 men in 10 months.

Celluloid is prepared by mixing pyroxylin plastics with camphor and a little alcohol and passing through heavy rolls. This transparent material is the basis of photo films, motion picture films, celluloid toilet articles, and other useful objects. Colored material may be incorporated when desired.

Synthetic camphor, made in the United States to the extent of a million pounds or more a year from turpentine, is the only rival to the Japanese monopoly in natural camphor; synthetic camphor forced a price drop for natural camphor from \$3.40 per pound to \$0.90 in a single year, and later to \$0.28. Camphor is indispensable in the manufacture of pyroxylin plastics such as celluloid (movie film, etc.). About 75,000,000 pounds of camphor are used yearly.

The automobile *lacquers* (Duco, etc.) contain cellulose nitrate (11.8 to 12.3 per cent nitrogen), resins, pigments, solvents, diluents, and plasticizers or softeners. Among the solvents are ethyl, butyl, and amyl acetates, methyl alcohol, and acetone. Glycol ethers have lately been added to this list.

Plasticizers, added to soften and give elasticity to the film, include dibutyl phthalate, tricresyl phosphate, and oxidized castor oil.

Cellulose Acetate. Cellulose, as already shown, reacts like an alcohol with acids or acid anhydrides because of its hydroxyl groups. With acetic anhydride it forms the useful ester called cellulose acetate. Worked into movie films by the aid of camphor or other plasticizer, this forms a product similar to the usual celluloid film but only slightly inflammable.

Cellulose ethers, as well as the esters, are finding considerable use as film formers.

Rayon. Manufacturers insist on use of the word "*rayon*" instead of "artificial silk" or "imitation silk." There are four types in use: cellulose nitrate, cellulose acetate, viscose, and cuprammonium.

Special weaves of rayon cord have largely replaced cotton cord in the manufacture of heavy truck tires.

Viscose rayon is made from wood cellulose by treatment of it with sodium hydroxide and carbon disulfide, forming first a yellow soluble compound called cellulose xanthate. This is aged, then spun into threads through spinneret holes only 0.003 inch in diameter, and decomposed by acid into the original cellulose, but with the silken luster desired. Viscose at present leads all other rayons in amount produced, being more than 65 per cent of the total. It is less durable than natural silk, but of course is far cheaper.

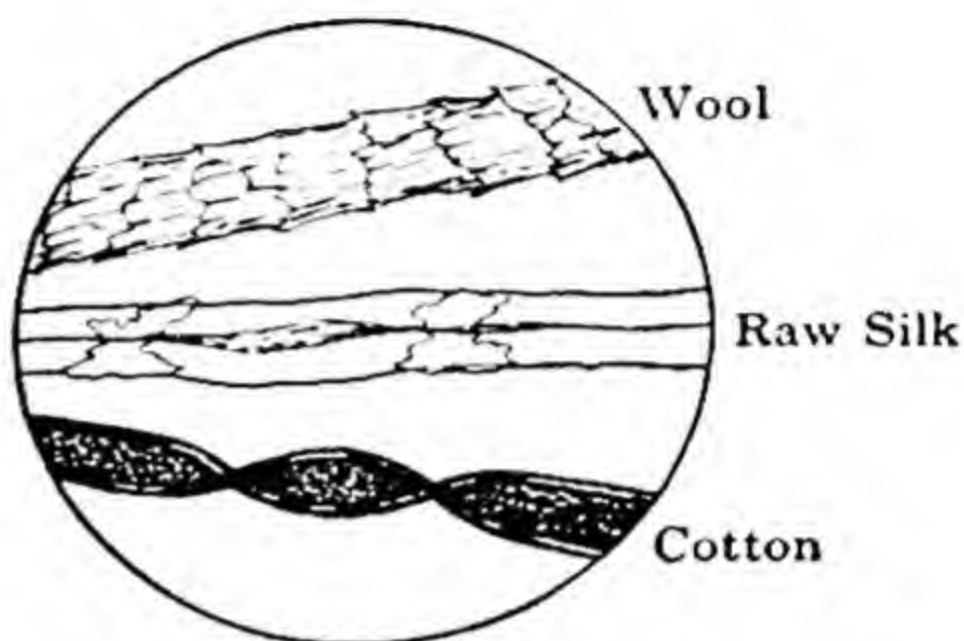


Fig. 173. Highly magnified fibers.

Our own rayon production in 1948 expanded to 900,000,000 pounds, and it is expected that this rate will increase. Great quantities are now used as tire cord.

Threads spun from a *cellulose nitrate* solution must be denitrated before use. *Cellulose acetate* threads may be catalytically hydrolyzed to reduce the number of acetate groups to yield the type of product desired.

Cuprammonium yarn (Bemberg) is prepared by spinning into an acid bath threads of a solution of cellulose in ammoniacal copper oxide. It is a very strong fiber.

Nylon. A new and very useful synthetic fiber called "Nylon" was announced late in 1938. Chemically it resembles natural silk, both being polyamides of protein-like structure. Basically it is derived from coal, air, and water. Elasticity and high strength characterize the finest fibers as used in hosiery, while a heavy fiber competes with hog bristles in the toothbrush

industry. Its use as parachute fabric, glider tow-ropes, etc., made nylon almost a military necessity.

Protein Fibers. There are 600,000,000 sheep in the world, yet wool is not cheap. Production of a synthetic wool from milk casein has greatly interested certain countries unable to raise

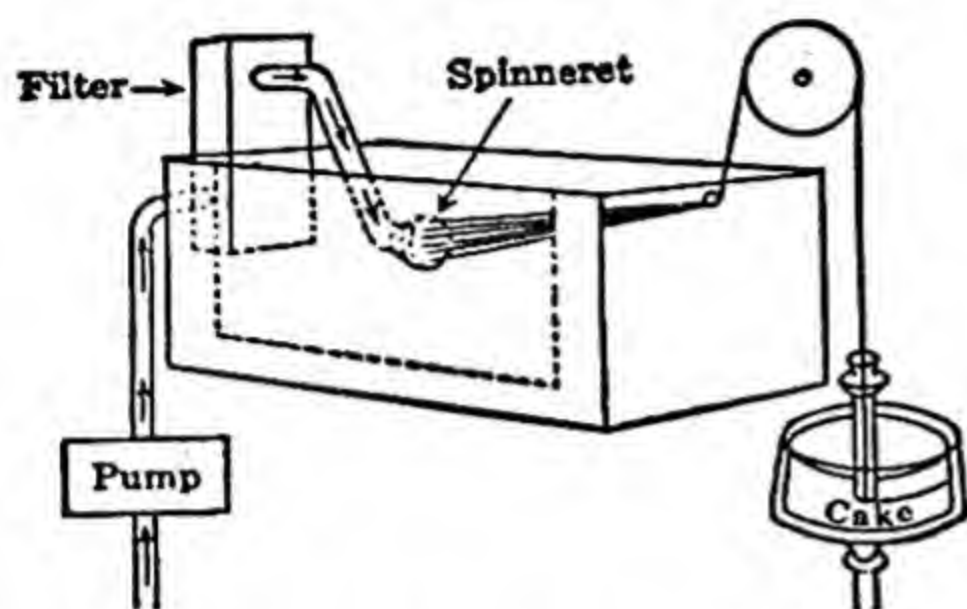


Fig. 174. Rayon solution forced through many small holes in a platinum disk (spinneret), coagulated as threads in an acid bath, and spun into lustrous thread. (Courtesy Colgate and Company.)

many sheep. This protein fiber is chemically unlike cotton (cellulose) but somewhat like natural wool and silk. It kinks, has the resilience of natural wool, and the ability to take wool dyes, but is weak when wet. Protein from soybeans or grain may also be converted into fibers as is possible with zein from corn.

There is enough surplus skimmed milk in this country

to make twice as much casein fiber as our wool consumption. Already it is used in certain blends.

Other Fibers. Spun-glass fiber is discussed on page 398. A synthetic silk-like fiber made from polyvinyl acetal resin, and known as Vinyon, is in commercial production. Vinyon fabrics are so resistant to acids and alkalies that they are used as filter cloths in industry. Saran fiber (see page 651) is very strong and chemically resistant. Research promises other fibers not yet offered for sale.

Recent progress in imparting flame-resistance, water-repellence, insect-repellence, and mildew-proofing and crease-proofing to textile fabrics, shrinkage-resistance to wool (upon washing), has been greater during the past war than in all previous time. Military needs in every climate have been stimulating to research.

DYEING

Of the three leading classes of natural fabrics, cotton, silk, and wool, the silk and wool are the easiest to dye. This is because their

fibers are protein material and more reactive chemically than the cellulose of cotton. Although 5000 dyes are known, only 1200 are used.

1. The Indigo Type. Solutions of dyes readily penetrate any fiber but wash out again unless the dye is held as an insoluble compound. For example, a fabric may be soaked in a solution of lead acetate and then in a solution of sodium chromate. Lead chromate is precipitated throughout the fabric and cannot be washed out. Indigo is insoluble in water. To get it into the fabric in the first place it is necessary to reduce it with sodium dithionite to the soluble, but colorless, indigo white. On exposing the fabric to the air this compound is oxidized to the insoluble blue indigo, now thoroughly entangled in every crevice and cell of the fibers. This dye, once natural but now synthetic, leads all others in tonnage.

2. Direct Dyes. Solutions of direct dyes diffuse into fabrics and either react with the fiber or are adsorbed powerfully on all surfaces. They are sometimes "salted out" or coagulated on and in the fiber by addition of sodium sulfate. Direct dyes for wool and silk are numerous, but for cotton they are relatively few.

The United States' annual production of synthetic dyes is 250,000,000 pounds, much of which is exported. Imports of a few special dyes reach 2 per cent of our total needs. Such independence, largely attained since 1914, adds to the national safety, for from the nature of things, dye plants and dye chemists can quickly be set at work making munitions of war and essential imported medicines.

3. Mordant Dyes. There are many beautiful dyes which are not retained by cotton without help from such "mordants" as aluminum hydroxide or tannic acid. Aluminum hydroxide is insoluble and hence cannot be worked into the fibers. However, if a solution of aluminum acetate penetrates the material, its natural hydrolysis can be increased by boiling, or a weak base may be added. By this device the insoluble aluminum hydroxide is formed throughout the fiber. A soluble dye penetrating below the surface is held by the hydroxide, so the dyed material becomes fast to washing. Other mordants are used, such as

chromium hydroxide or even tannic acid. The latter material forms insoluble tannates with basic dyes such as methylene blue. Mordant action can be demonstrated in a test tube. To a solution of alum and a dye add a base. Filter and wash the precipitate. It retains the dye. Such compounds are called *lakes* and in dyeing they are formed in the fiber.

Two thousand or more years ago only royalty could wear Tyrian purple, a color developed when a fluid secreted in minute quantities by a snail-like shell-fish (*murex*) was exposed to sun and air. Yet this "royal purple," a di-brom derivative of indigo, is now surpassed in quality by synthetic di-brom indigo sold cheaply.

PLASTICS OR SYNTHETIC RESINS

All plastic materials are molded to desired shapes by the use of heat (to soften) with attendant pressure ("thermoplastic"), or by shaping a reactive fluid mixture and setting it to the desired form with the aid of heat, pressure, and, possibly, a catalyst ("thermo-setting").

Celluloid, the earliest plastic, resulted from an effort in 1868 to make a good substitute for ivory in the making of billiard balls. Hyatt, the inventor, was discouraged but he did not then foresee the enormous uses of transparent celluloid — movie film, for example. The dangerous inflammability of this cellulose nitrate material led to development of cellulose acetate film, the "safety film" used in homes and schools.

The 1909 invention of *bakelite* (phenol-formaldehyde resins) opened up new paths for chemists. It had great commercial success as material for telephone receivers, handles for toilet articles, buttons, fountain pens, pipe stems, electric insulation, and hundreds of familiar articles. Naturally imitations and developments followed.

The *urea-formaldehyde* resins or plastics take colors well, have reasonable breakage resistance and therefore find use as cheap table ware.

The *vinyl* resins, and the closely related *vinylidene* resins are the result of the polymerization of simple molecules (linking them together in chains given strength by cross-chain bonds). Since one

of these resins is tasteless, odorless, and harmless, it is in considerable use as a thin film lining of food containers and beer cans.

One of the vinyl plastics, in flexible form, is said to make an excellent inner tube for rubber tires because it is absolutely impervious to air.

Saran (Polymerized vinylidene chloride) is a recent arrival with great promise. It can be formed into strong fibers for fabrics or molded into pipe resistant to concentrated acids, alkalies (except ammonia), and many other chemicals. With restrictions on the use of metals, as in wartime, saran may be used for plumbing. Strong flexible films of saran, water-resistant, are used for wrappings.

Such modified rubber plastics as *pliofilm* in thin, tough, transparent sheets protect fresh fruit and other foods to a remarkable degree. In the near future pliofilm in particular will profoundly influence world trade in perishable foods. It is rat-proof, vermin-proof, tasteless, and odorless. **Koroseal** (polymerized vinyl chloride) substitutes for rubber in such material as raincoats, umbrellas, shower curtains, hospital bed-sheeting, and table cloths.

Plywood, thin sheets of wood bonded under pressure and heat with waterproof plastic glues, is already in great use for the construction of airplanes, light boats, portable houses, etc. One type of plywood, in proportion to weight, is stronger than some alloy steels.

Dielectric heating of plywood layers greatly speeds up the setting of the plastic bond (minutes instead of hours) because heat is generated instantly and uniformly throughout the mass by the high-frequency electric current (several million cycles per second).

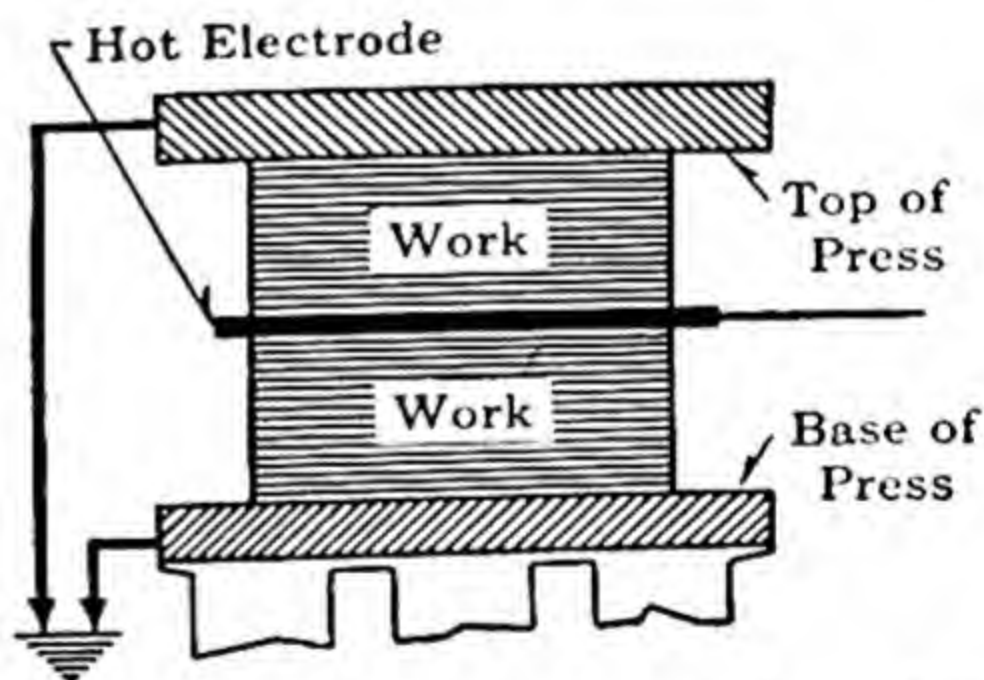


Fig. 175. Dielectric heating of plywood in a high-frequency field between two metallic surfaces having a relatively high difference of potential between them. (Courtesy Chemical Industries).

TYPES OF PLASTICS

Formaldehyde Group	<ol style="list-style-type: none"> 1. "Bakelite," etc. Product of formaldehyde + phenol 2. Variation of above. Formaldehyde + other phenols 3. Variation of above. Other aldehydes + phenol 4. Casein plastics. Formaldehyde + casein of milk 5. Other protein plastics. Formaldehyde + protein of soybeans 6. Urea plastics (Beetle, Plaskon, etc.). Formaldehyde + urea 7. Melamine plastics. Formaldehyde + melamine
Cellulose Group (Esters, except 4)	<ol style="list-style-type: none"> 1. Celluloid. Cellulose nitrate + camphor 2. Variation of above. "Tenite," "Lumarith," etc. Cellulose acetate + camphor 3. Variation of above. Cellulose acetate-butyrate 4. Ethyl cellulose (an ether). Oil-resistant and tough
Vinyl Group	<ol style="list-style-type: none"> 1. Polyvinyl acetate or butyral or chloride 2. Polyvinyl acetate-chloride 3. Polyvinyl acetal ("Butacite") 4. "Saran" (from vinylidene chloride) 5. "Koroseal" (from vinyl chloride) <div style="display: flex; align-items: center; margin-left: 600px;"> <div style="text-align: center; margin-right: 10px;"> $\begin{array}{c} \text{Cl} \quad \text{H} \\ \quad \\ \text{C}=\text{C} \\ \quad \\ \text{H} \quad \text{H} \end{array}$ </div> <div>is vinyl chloride</div> </div> <div style="display: flex; align-items: center; margin-left: 600px; margin-top: 10px;"> <div style="text-align: center; margin-right: 10px;"> $\begin{array}{c} \text{Cl} \quad \text{H} \\ \quad \\ \text{C}=\text{C} \\ \quad \\ \text{Cl} \quad \text{H} \end{array}$ </div> <div>is vinylidene chloride</div> </div>
Other Plastics	<ol style="list-style-type: none"> 1. "Plexiglas" or "Lucite." Methyl methacrylate 2. Nylon (from adipic acid, etc.). Sheet form 3. Polystyrene (from ethyl benzene, etc.) 4. Pliofilm (rubber hydrochloride) 5. Alkyd resins (from glyceryl phthalate and linoleic acid). "Glyptal," etc. 6. Vistanex (polymerized isobutylene) 7. Butalyn, Amberol. Modified natural rosin plastics 8. "Polythene." Ethylene polymer. Resists H_2O and all solvents 9. "Teflon" (polytetrafluorethylene). Resistant metal coating

The above plastics or synthetic resins are selected from a large and rapidly growing list.

Melamine resins give wet strength to paper and shrink-proofing to wool.

The new water-emulsion paints depend upon the quick drying, or setting, of *alkyd resins*. These paints are excellent for porous

surfaces, require a minimum of organic solvent, or none, and yield very good protective films for indoor surfaces.

By 1948 United States production of all plastics, not including rubber, reached the great annual total of 1,250,000,000 pounds and production is rapidly increasing. Vinyl resins lead with alkyd, cellulose acetate plastics, and the phenolic resins in large production.

Exercises

1. What is the greatest crop in the world? Why?
2. What natural fiber does Nylon most closely resemble? Influence of Nylon on world affairs?
3. With what materials do plastics compete? Will they ever be used for the bodies of autos?
4. What was the earliest plastic made? The second?
5. If cotton ceased to grow, would the important derivatives of cellulose be impossible?
6. What are the protein plastics?
7. What are the uses of pliofilm?
8. Name five synthetic fibers.
9. How is urea used in plastics? Phenol?
10. What is polythene? What are its possible uses?
11. What is the explosive cordite? Dynamite? Guncotton?

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Chapter 57 FOOD AND NUTRITION. CHEMOTHERAPY

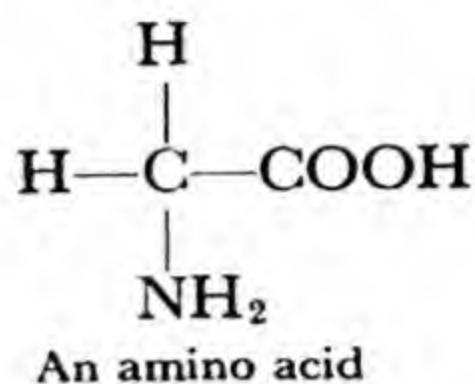
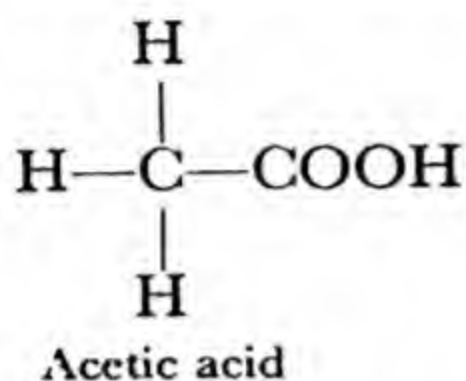
Food is needed by the animal body to replace worn-out tissues, to provide for growth in the young, and to supply heat to maintain the body temperature. Of course food is the source of all the bodily energy. When a muscle contracts tissue is oxidized and heat liberated. It has been definitely proved that the body is a very efficient sort of engine. Practically the same amount of energy in the ultimate form of heat is liberated when we eat and digest food enough to produce, say, 100 grams of carbon dioxide in the exhaled air as when enough coal is burned under a boiler to produce 100 grams of carbon dioxide. The average adult exhales 1100 grams of carbon dioxide, excretes 25 grams of urea, and large quantities of hydrogen and oxygen in the form of water, daily. Protein is finally burned to urea while starch, sugar, and fats are burned to carbon dioxide and water. An alcohol lamp burning a pint a day is as large a source of heat or other form of energy as an average man.

Classification of Foods. In addition to water and air, the human body requires food from four great classes.

Proteins we get in lean meat, milk, cheese, eggs, beans, peas, and the cereals. The average protein molecule is very large and very complex, and has a probable molecular weight of several thousand. Proteins contain nitrogen, carbon, hydrogen, oxygen, and may contain sulfur.

Different proteins are built up from nearly 30 different amino acids (organic acids containing the basic NH_2 group) and although a few of these acids may be synthesized from others in the

body, the majority must be supplied in the diet. Methionine, one of the two amino acids containing sulfur, is essential to life, and lysine to growth. So proteins lacking such amino acids are incomplete and must be balanced in the diet by other proteins. White bread lacks lysine unless considerable milk is added in the baking as is now done with the best of the commercial breads. We now know that ten amino acids in proteins are essential.



Fats are found in meat, milk, nuts, and the oils expressed from corn, cottonseed, peanuts, coconuts, and soybeans.

Carbohydrates are found as starch in the cereals, in rice, potatoes, chestnuts, and various tubers, and as sugars in cane, beets, fruits, and other products.

Mineral salts, or compounds, particularly those of iron, calcium, copper, manganese, phosphorus, and iodine, are obtained from milk, eggs, legumes, nuts, chocolate, vegetables, meats, and whole grains.

In listing food requirements it is important not to overlook the vitamins so necessary to growth and vigor, or the cellulose roughage needed to give bulk and to keep the digestive material moving along.

THE CHEMICAL COMPOSITION OF MAN

Oxygen	65	per cent	Sulfur	0.25	per cent
Carbon	18		Sodium	0.15	
Hydrogen	10		Chlorine	0.15	
Nitrogen	3		Magnesium	0.05	
Calcium	1.5		Iron	0.004	
Phosphorus	1.0		Mangarese	0.003	
Potassium	0.35		Iodine	0.00004	

Data from Sherman

Digestion. It is a strange fact that animals are unable to assimilate the very simple foods that nourish plants. And yet the

carbon dioxide, nitrates, ammonia, and potassium salts so relished by plants are soluble, whereas, with the exception of sugars, and urea for cattle, food for animals is insoluble and must be made soluble by the process of digestion before it can be transported throughout the body tissues.

Proteins	<ul style="list-style-type: none"> Partly broken down in the stomach by <i>pepsin</i> Completely torn apart in small intestine by <i>trypsin</i> and <i>erepsin</i> Products carried through intestinal wall to all parts of body Products built up again into tissue
Fats	<ul style="list-style-type: none"> Emulsified into minute droplets by <i>bile</i> in the small intestine Split by <i>lipase</i> into fatty acids and glycerine Products pass through intestinal wall with aid of bile salts Transported and built into fats again Oxidized as a fuel for energy
Carbohydrates	<ul style="list-style-type: none"> Starch partly digested by <i>ptyalin</i> of saliva Starch converted (by <i>amylase</i> of intestine) into malt sugar (maltose) Maltose → glucose (by <i>maltase</i>) Glucose passes through intestinal wall Glucose oxidized as fuel for energy Cane sugar split by <i>sucrase</i> of the intestine into glucose and fructose

In the outline above, the enzymes of the digestive fluids are printed in heavy type. It is not essential that you commit their names to memory, but you should know something of the general processes of digestion.

The Fuel Value of Food. One gram of fat burned in the body yields 9 Cal. (1 Cal. = 1000 cal.), and it yields but little more when actually burned with flame in a calorimeter. From the analysis of any given food one can readily compute the energy value of a pound or kilo of that food. The fuel values given here are, perhaps, a trifle too low:

$$\text{Fuel values} \begin{cases} 1 \text{ g. fat} = 9 \text{ Cal.} \\ 1 \text{ g. protein} = 4 \text{ Cal.} \\ 1 \text{ g. carbohydrate} = 4 \text{ Cal.} \end{cases}$$

The Balanced Ration. A man of average activity should obtain daily from his food about 3000 Calories of energy; 75 grams of proteins, 80–90 g. of fat, 400–500 g. of carbohydrate, 0.68 gram of calcium, 1.32 grams of phosphorus, and 0.015 gram of iron.

However, the energy demand varies with the weight of the individual and with the amount of exercise taken. A growing youth requires more in proportion to weight and exercise.

A varied diet, stressing milk and fresh vegetables, is the best. The utilization of fats is greatly aided by carbohydrates. More starch can be tolerated than sugar.

The mineral salts, which it seems unwise to leave to chance in the diet, are compounds of iron, calcium, phosphorus, and iodine.

Iron is essential to the red hemoglobin of the blood (although copper takes its place in the blue blood of lobsters); calcium to bones, teeth, and the blood; phosphorus to bones, teeth, nerves, brain and, in fact, to every cell in the body. A man of average weight has, in his tissues and bones, 3 grams of iron, 1.4 pounds of phosphorus, and 2.3 pounds of calcium. A trace of copper seems to help him utilize iron; a little iodine (combined) is vital to the function of the thyroid gland (in the neck); and both manganese and magnesium are essential in very small amounts. Sodium chloride is not a mere seasoning and preservative for foods; it is needed in the blood and in the formation of the hydrochloric acid of the gastric juice. Liver, nuts, legumes and sea food are our richest sources of copper; milk is the best source of calcium.

"Unless at least a pint of milk a day per person is used in a community serious nutritional errors are certain to develop and affect the vitality, sturdiness, and capacity to resist disease of a large number of both children and adults." — Prof. Henry C. Sherman, Columbia University.

Prolonged boiling of vegetables in excessive volumes of water — and draining off this water — is to blame for a great *loss of valuable mineral salts* and some vitamins. Cooking by steaming might save this loss and the use of a minimum of water would help.

Yet after all precautions are taken to secure the right number of calories, adequate proteins, and sufficient calcium, iron, phosphorus, roughage, sodium chloride, and even the little sodium iodide needed to prevent goiter, a person may waste away for lack of vitamins.

Much research, in recent years, has been put into the problem

of producing a palatable yeast as protein food. Dried yeast is 50 per cent protein and if grown on cane molasses the yield per acre is several times that of the next best protein crop — soybeans.

Vitamins. Many dietary observations since 1897 led to the discovery that animals require for growth and health very small quantities of certain accessory food substances not recognized by ordinary analysis of animal tissues. These accessories, practically unheard of before 1911, we call *vitamins*. Their methods of functioning are not yet fully understood. At least eight or ten are well known, and several others are being studied. Several have been synthesized in quantity, greatly reducing costs and increasing the amount available.

Diets composed essentially of bread, meat, potatoes, sugar, and fats other than butter are likely to contain too little of vitamin A. Unfortunately such diets are all too common. For that matter, such a diet is deficient in the other vitamins and in salts; so it may well be considered unsafe.

Carotene (provitamin A) is a red compound, $C_{40}H_{56}$, soluble in fats but found in very few of them. Plant food, such as carrots and green, leafy vegetables, actually contains no vitamin A whatever, but may contain carotene, which man converts in his body into vitamin A. The cow makes this transformation for us and deposits some of the vitamin in milk much as the hen deposits it in the egg yolk — and very small fish of the sea synthesize it for voracious halibut, cod, tuna, salmon, and other larger fish to store in their livers. The new synthetic vitamin A has not yet reached the commercial stage.

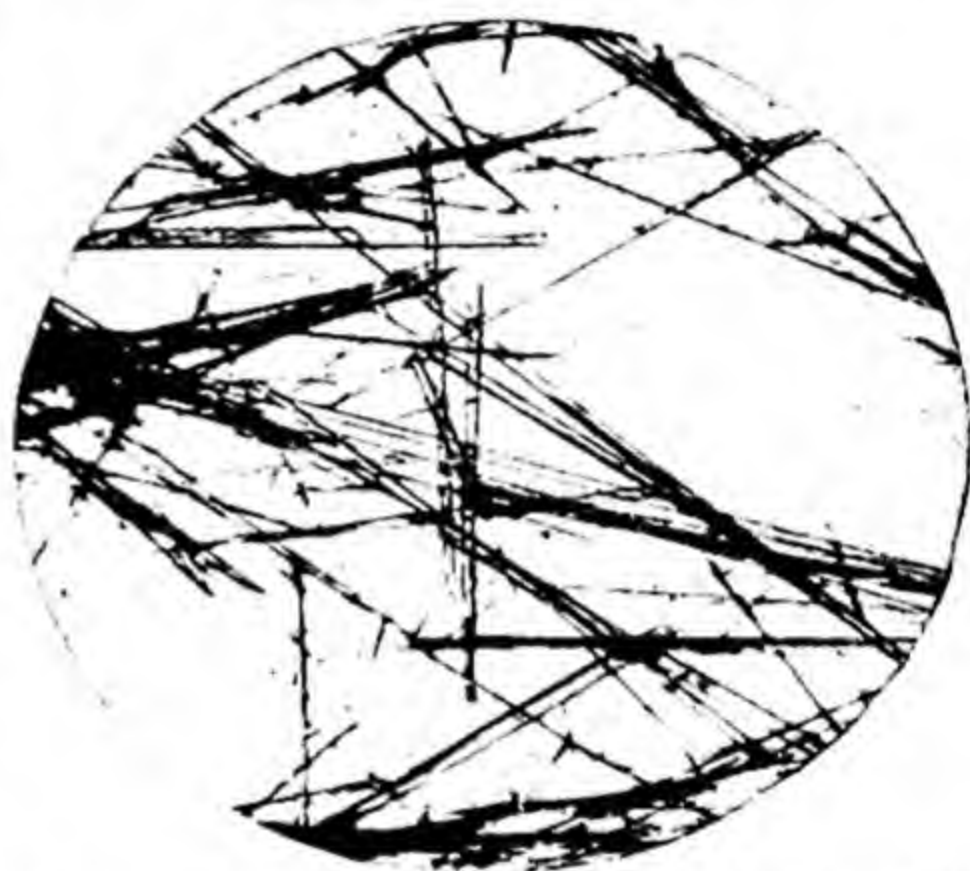


Fig. 176. Crystals of lemon-yellow vitamin A (the alcohol) containing one molecule of CH_3OH of crystallization. Isolated in 1936. Holmes and Corbet, *J. Am. Chem. Soc.*, 59, 2042 (1937).

Shark liver oil averages nearly 40,000,000 units of vitamin A per pound. The average man needs only 5000 units daily in his food.

Losses in Storage and Cooking. There is some loss of vitamins from foods due to the action of oxygen and light. This loss is serious in the case of ascorbic acid, vitamin C, which is very sensitive to oxidation. The water-soluble vitamins (B complex and C, etc.) may be lost along with minerals if water in which vegetables are cooked is thrown away. It should be saved for soups and drinks.

Unfortunately, 90 per cent of the vitamin B in whole wheat is lost in the milling process when white flour is produced. The campaign to "enrich" this flour by restoring the lost B₁ and G and, perhaps, iron and calcium, is succeeding. More than 40 per cent of our flour is now enriched.

The "B complex" consists of a dozen vitamins but of these only B₁, G (riboflavin) and niacin are well known to the public. Yeast is a rich source of the "B complex."

A great deal of milk for children is "irradiated," treated with the proper wave-length of ultra-violet light in order to give it a substantial amount of vitamin D, the bone builder.

Vitamin K, an antihemorrhagic factor, is of value in some cases of bleeding.

GOOD SOURCES OF VITAMINS

Vitamin A and Carotene	<ul style="list-style-type: none"> Butter, milk, eggs, carrots, green leafy vegetables, tomatoes, sweet potatoes, green peas, liver, and fish liver oils Capsules of fish liver oil concentrates Carotene, C₄₀H₅₆, of plants (converted into A by animals)
Vitamin B ₁ (Thiamin)	<ul style="list-style-type: none"> Outer layers of grains, wheat germ, yeast, lean pork, vegetables Now synthesized by the ton
Vitamin C (Ascorbic acid)	<ul style="list-style-type: none"> Citrus fruits, raw cabbage and raw spinach, green peas, tomatoes (fresh or cooked), melons, and various fresh fruits and vegetables Now synthesized from glucose by the ton
Vitamin D	<ul style="list-style-type: none"> Liver oils. Very little in ordinary foods. Outdoor sunshine converts ergosterol of skin into vitamin D "Viosterol" (synthetic D) now synthesized from a chemical in yeast

Vitamin G (Riboflavin)	{ Milk, eggs, liver, potatoes, spinach, asparagus, kale, grape- fruit, and yeast Now synthesized
Niacin (Nicotinic acid)	{ Liver, kidney, lean meats, fish, milk, green leafy vegetables Synthesized at low cost

VITAMIN INFLUENCES

Vitamin A $C_{20}H_{29}OH$	{ Aids growth, general health, resistance to disease Prevents night-blindness (important in driving at night) Often helpful in eye strain caused by fine mechanical work
Vitamin B ₁ (Thiamin) $C_{12}H_{16}ON_4S$	{ Prevents beriberi, promotes appetite, tones up digestive system, and builds up vigor and morale
Vitamin C (Ascorbic acid) $C_6H_8O_6$	{ Prevents scurvy and is necessary to sound teeth and healthy gums Aids wound healing, is helpful in shock, builds up resistance to disease Extra amounts of 200–500 milligrams (or more) daily often help in hay fever and other allergies
Vitamin D $C_{28}H_{43}OH$	{ Prevents rickets Necessary to sound bones and teeth
Vitamin G (Riboflavin) $C_{17}H_{20}N_4O_6$	{ Aids growth and general health
Niacin (Nicotinic acid) $C_6H_5O_2N$	{ Practically prevents pellagra

CHEMOTHERAPY

Vitamins and hormones are alike in regulating the body processes. However, we get our vitamins in our food and synthesize our own hormones, such as insulin and thyroxine.

Thyroxine, the potent hormone of the thyroid gland, is 65 per cent iodine. It has been isolated and synthesized. Kendall extracted only 35 grams of thyroxine from 3 tons of fresh thyroid glands, so it is fortunate that it can be synthesized.

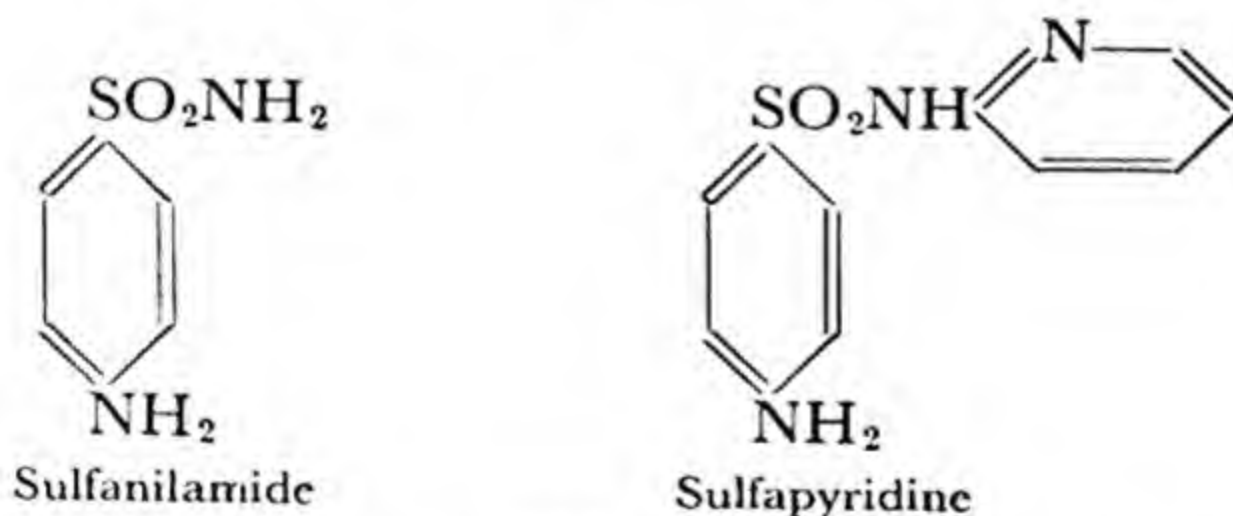
Adrenaline is present in blood plasma to the extent of 1 part in 20,000,000, yet it is a powerful regulator of the sympathetic nervous system. The sex hormones, too, are proving to be great aids to the physician. Butenandt extracted only 13 mg. of one from 25,000 liters of urine.

Synthetic medicines like sulfanilamide, sulfapyridine, sulfadiazine, and other "sulfa drugs" are doing wonderful service in the treatment of pneumonia and several other diseases. In a



Fig. 177. Crystals of sodium penicillin, X 90. (Courtesy E. R. Squibb and Sons).

recent five-year period they reduced the death rate from pneumonia to 30 per cent of its previous value. Penicillin, rivaling sulfa drugs, has been isolated from a mold. See page 639. Several other "antibiotics" have been produced from molds.



In the above diagrams a CH is understood at each corner of the benzene hexagon (unless otherwise shown).

There are 50,000,000 sufferers from malaria in the world and at least 3,000,000 deaths from it yearly. There will never be enough quinine to treat all these patients (and it does not cure), so tremendous and successful efforts were made to synthesize better anti-malarials.

In contrast to helpful medicines the lot of man has been vastly improved by such "killers" as ANTU (alpha naphthylthiourea), the most useful rat poison, and DDT, toxic to mosquitoes, flies and other dangerous insects.

Improvements on morphine give great promise. Chemotherapy is a fertile field for research.

Exercises

1. If you have access to a food chart, make out a menu for the three meals of the day, tabulating the weight in grams of each portion as nearly as can be estimated, the percentage of fat, protein, and carbohydrate and the total fuel value of each portion. The total for the day must be 3000 Cal. and about 75 g. of protein must be included. The calculations must be based upon the analyses given in the table. More extensive tables are found in books by Sherman and Eddy given in the following list of references. In Rose's *Feeding the Family* may be found a table giving the weight of 100-calorie portions of various foods and another giving calories per pound.
2. How can we test a food for vitamins?
3. Why is not one protein as good as another?
4. What is an enzyme? Have you any with you?
5. Name five foods that are rich in three vitamins.
6. What are the best food sources of calcium, phosphorus, manganese, copper, and iron?
7. What finally becomes of the protein nitrogen in the body?
8. Give the weights of carbohydrate, protein, and fat which would supply a menu, such that the total food value was 3000 Cal., that 75 g. of protein was included, and that the remaining fuel value was divided equally between carbohydrates and fats. Consult tables in books on nutrition.
9. What cooking losses occur with vitamins?
10. What are the food sources of vitamin A and carotene?
11. What is the cause and meaning of "night-blindness"?
12. What vitamin deficiencies are associated with scurvy? Beriberi? Rickets? Pellagra?
13. What important vitamins have been synthesized?
14. How are you cheating yourself if you eat white bread? What do you propose to do about it?
15. What vitamin helps victims of hay fever and food allergies?

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Chapter 58 RADIATION CHEMISTRY

Science includes in the electromagnetic spectrum rays that affect the eye and others such as the ultra-violet, X-rays, and infrared which affect the photographic plate. The term light is further extended by physicists to include heat rays and wireless waves.

Wave lengths are expressed in millimicrons, $m\mu$, or in Ångström units (\AA).

$$1\ m\mu = 1\ \text{millionth of 1 millimeter,}$$

$$1\ m\mu = 10\ \text{Ångström units}$$

The extreme wireless (radio) waves may be expressed in terms of kilometers, yet signals have been sent with waves as short as one centimeter. The wave lengths of visible light range from 400 $m\mu$ for the shortest violet to 800 $m\mu$ for the longest red, a light octave somewhat analogous to the octave in music, based on a doubling of vibration frequency. The velocity of all light radiation is the same, hence there is an obvious relation between wave length and the number of vibrations per second (vibration frequency). Lemon states that if we call the range of visible light one octave, the known radiation range is 60 octaves. The diagram on page 666 (not drawn to scale) represents this range.

The Octaves of Light. The electrical nature of light was first clearly postulated by Maxwell in 1873 and confirmed in 1888 by Hertz, who created electric waves of the type now used in radio, with properties similar to visible light waves. The former gap between radio waves and visible light has now been bridged,

working from both ends. X-rays arise when electrons, radiating with lightning-like speed from the cathode in a high-vacuum electric discharge tube (p. 299), strike a plate of metal (usually a tungsten "target"). Gamma rays, emitted from radium and similar elements, are similar but shorter in wave length.

The effects observed in connection with cosmic rays seem to be due, in part, to radiation of wave lengths still shorter than the gamma rays.

Matter Waves. A beam of light, once thought to consist of waves, is now said to act in certain respects like waves and in

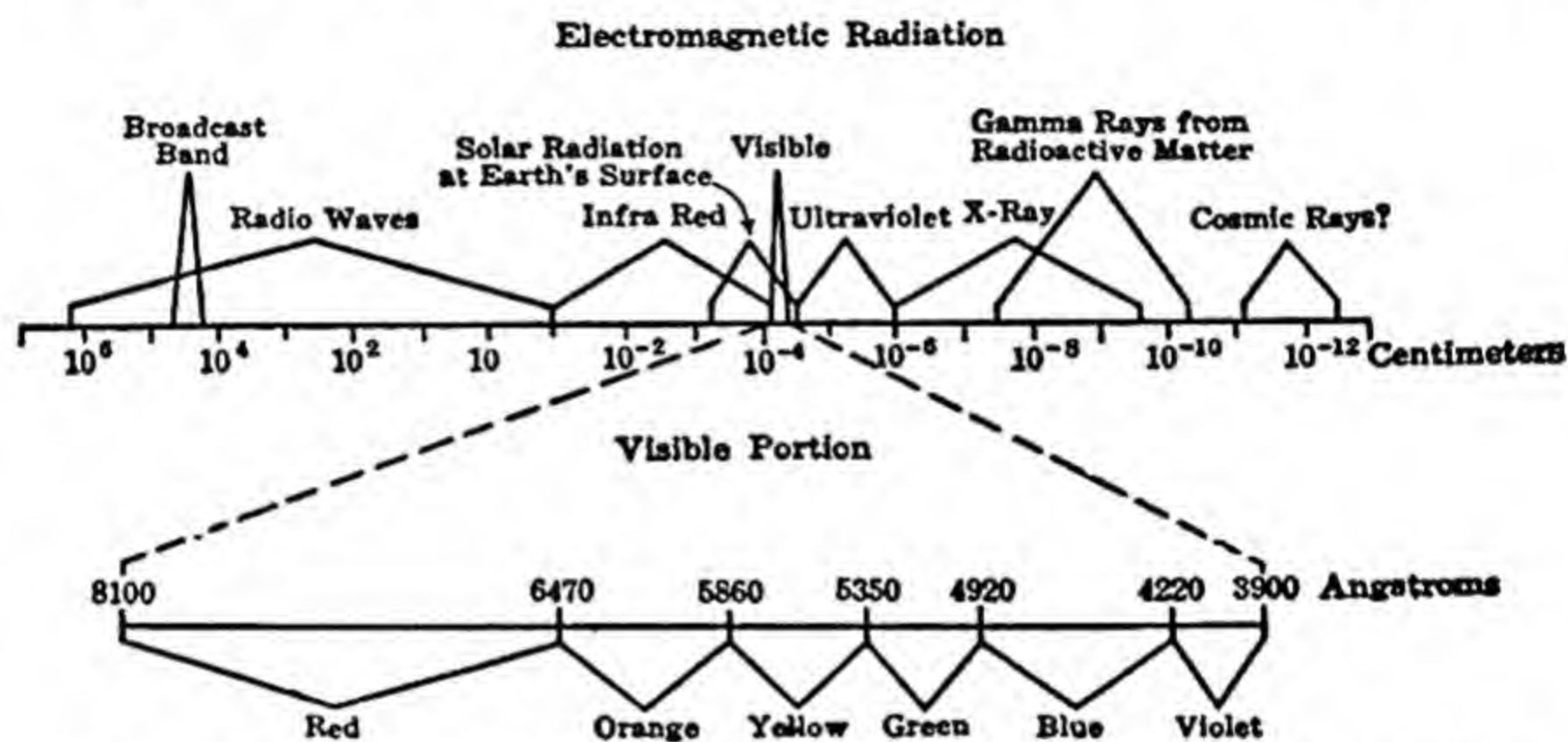


Fig. 178. The range of electromagnetic radiation. (Courtesy Smithsonian Institution, 1933 Report.)

other respects like a stream of particles. "Photons" are corpuscles of light. Similarly a stream of electrons has shown diffraction (formerly supposed to be characteristic of waves) and now beams of ionized atoms show diffractions. A stream of hydrogen atoms fired at a crystal of lithium fluoride was diffracted so that the wave length of the flying atoms was calculated. This atom-wave (not identical with a light wave) is very short, approximately the diameter of an atom.

The wave length of these matter waves depends upon the velocity and mass of the particle. Diffraction patterns, states Davissohn, produced by a beam of high-speed electrons passing through a film of silver are recorded on a photographic plate in rings in exactly the pattern calculated from the crystal structure

of silver and the assumption that the electron beam is a beam of monochromatic X-rays.

Electron Beams. Inventors have developed an *electron microscope*, with far greater power than previous instruments, using electromagnets or electric fields to focus the electrons. If these

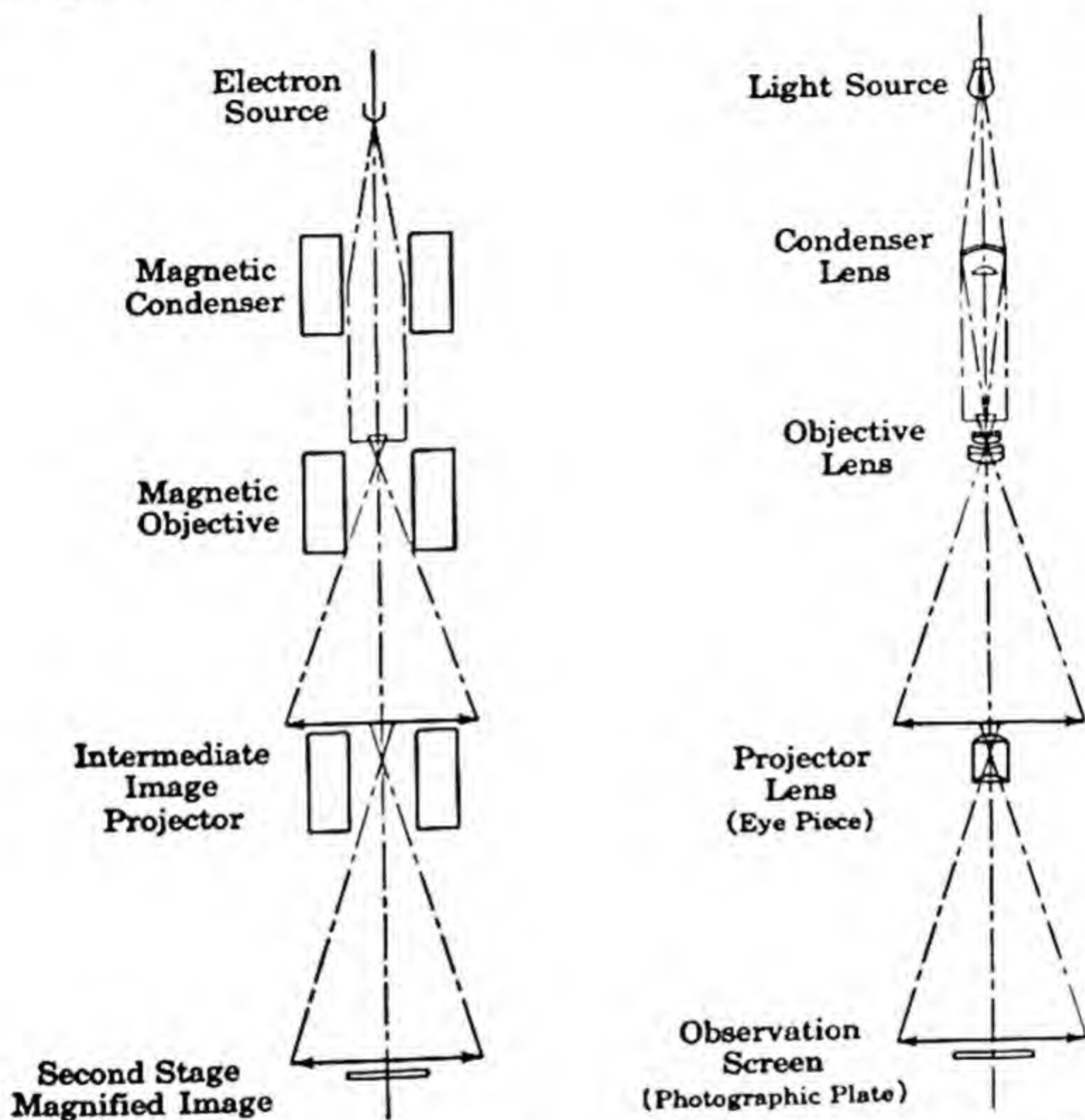


Fig. 179. The RCA electron microscope is here represented diagrammatically in comparison with the common microscope using visible light. A beam of electrons of high velocity (at voltages from 30,000 to 100,000) takes the place of ordinary light.

electrons hit a fluorescent screen of zinc sulfide they will be made visible, in a sense, by the light flashes or glow on the screen.

In the electron microscope a beam of high-velocity electrons takes the place of light. The electron rays are converged by a magnetic condenser (instead of the usual lens) onto the specimen. The beam passing through is focused by a magnetic objective to form a first image, enlarged about 1000 times. The projector-lens

coil then magnifies this image about 250 times to reach a final value of 25,000. This enlarged image can be viewed directly by aid of a fluorescent screen or it can be recorded on a photographic plate. Photographic and screen enlargement may be effective up to 100,000 diameters or more. Hitherto the limit of magnification had been 5000 diameters. Streptococcus germs, viruses, and



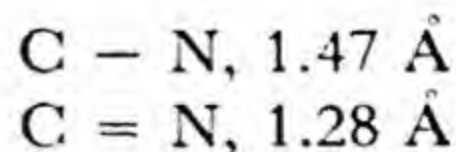
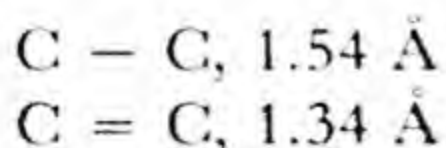
Fig. 180. Electron microscope photograph of zinc oxide smoke, X 42,000. (Courtesy Stamford Research Laboratories, American Cyanamid Co.)

the larger organic molecules take on new meaning under such new microscopy.

Debye has been getting bull's-eye ring pictures of molecules by shooting 30,000-volt electrons down a small vacuum chamber where they pass through molecular gases to be studied. These gases scatter them into rings whose size depends upon the interatomic

distances in the molecules. Such electron waves correspond to 0.05 of one Angström unit of length.

By measuring the diffraction patterns of electron beams shot through the vapors of various substances the distances between atoms in complex molecules have been determined. When these distances are found to be abnormal for a given pair of atoms an oscillating or resonating structure is indicated. Similar patterns obtained with crystalline solids have made possible an understanding of the lattice structure. The C-C distance in the benzene ring averages 1.39 Angström units, yet the influence of single and double bonds must be noted.



An electron beam can crack some hydrocarbons into smaller molecules.

Light Quanta. Radiant energy comes to us in little packets or quanta which vary with the wave frequency of the light. The

longer waves such as red have smaller quanta than the shorter such as violet. In fact X-rays, gamma rays, and cosmic rays with the shortest wave length of all have almost infinitely larger quanta than visible light. In other words the value of the quantum is directly proportional to the vibration frequency,

$$E = hv,$$

where E is the energy of a quantum, h is the Planck constant, and v is the frequency.

ENERGY OF RADIATION

(One electron-volt represents the energy of one electron that has fallen through a difference in potential of one volt)

Photons from an electric lamp	2 electron-volts
X-rays	20,000-100,000 volts
Gamma rays (from protactinium)	2,500,000 volts
Cosmic rays	6,000,000,000-10,000,000,000 volts

The photoelectric effect of X-rays or ultra-violet rays on metals strengthens this conception. The velocity of the electrons torn loose from metallic surfaces by these radiations has no relation to the mere intensity or brightness of incident light (the greater the intensity the greater the number of electrons torn loose) but changes only with the color (vibration frequency) of the light. Presumably a single light-quantum is used up in liberating a single electron from the metal.

Photochemical Reactions. The electrons rotating around the nucleus of an atom are considered to exist at different energy levels. An atom is said to be in an "excited state" when one or more electrons are out of their normal energy levels, displaced farther from the nucleus by radiant energy from without or by collisions. When such misplaced electrons return to their normal energy levels light is emitted, its frequency of vibration depending upon the energy difference or energy levels through which the electron falls back. The transition is always abrupt, or in steps, "quanta."

These excited or activated atoms can take part in chemical reactions to which they were previously indifferent. It has long

been recognized that it is only the absorbed light that influences chemical reaction. Photographs of the spectra secured when light passes through the substance to be studied may show an absence of certain usual lines. This indicates absorption of energy corresponding to the light vibrations responsible for such spectral lines. When such energy is absorbed some molecules of the illuminated substance must be made more active.

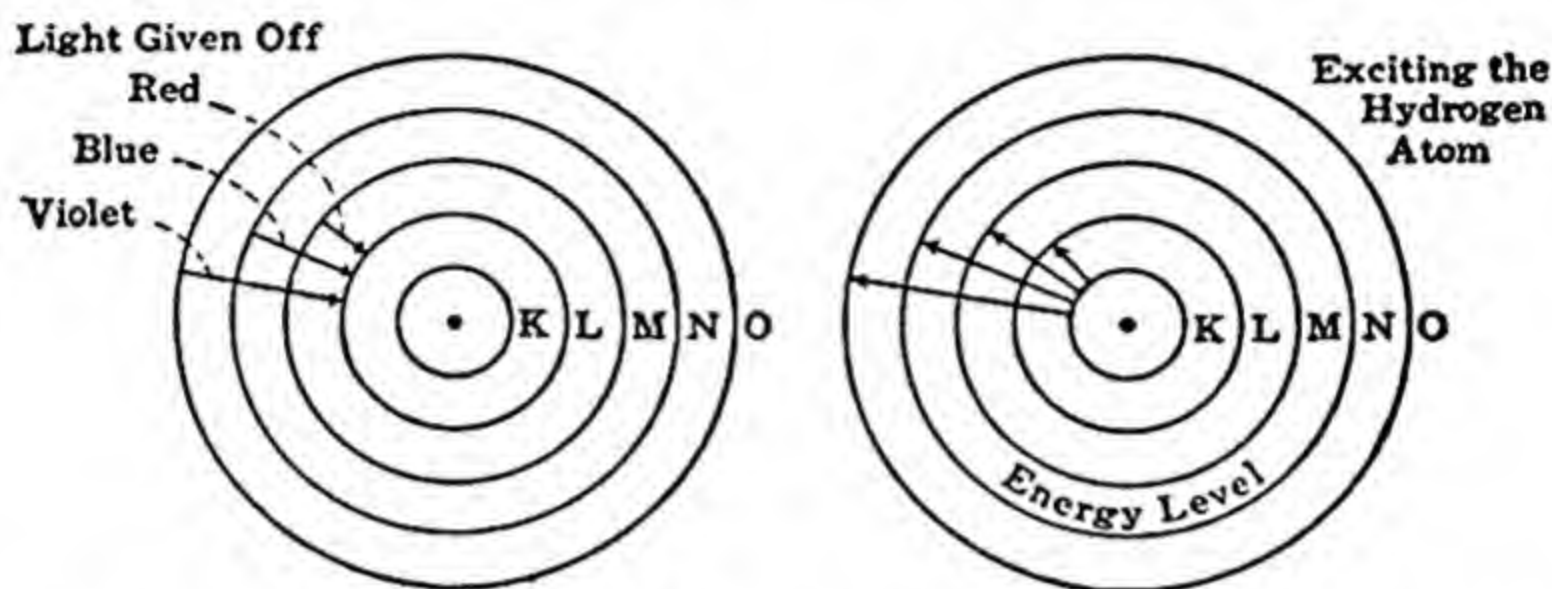


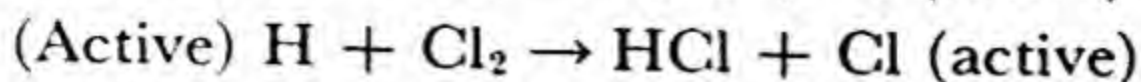
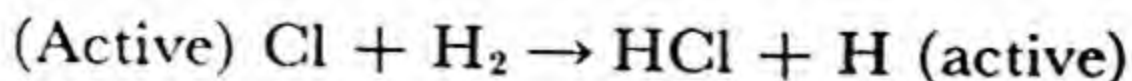
Fig. 181. On the right an atom is excited by some outside energy (light, heat, X-rays, electron bombardment, etc.) and electrons are displaced to energy levels farther from the nucleus. If over-excited the atom may lose an electron and become an ion. On the left an excited atom radiates light as the displaced electrons fall back to lower energy levels. If an electron returns all the way to the inner K level ultra-violet light is radiated.

Two substances, otherwise unreactive under the influence of radiations that they do not absorb, may often be made to react by addition of a third substance that does absorb some of the light energy. Such substances, sensitizers, as they are called, are found among the dyes and used in photography.

Mercury vapor may readily be activated or excited by radiation.

If an excited mercury atom collides with a hydrogen molecule, part of the energy of excitation can be used to dissociate the molecule into hydrogen atoms which become excited.

Chlorine molecules are dissociated to some extent by light and the very reactive chlorine atoms may then attack the hydrogen molecule as shown in the following equation.



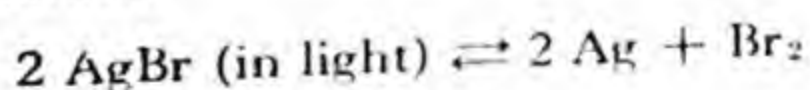
Obviously a few active chlorine atoms may go on like this, causing the formation of a great deal of HCl, a typical "chain reaction."

Reactions in which a series of processes results from the primary activation of one molecule are called *chain reactions* (Not confined to photochemistry.) Uranium fission is a chain reaction.

Photography. Photography, modernized picture-writing, is an essential tool for the astronomer, and is now coming to the aid of surveyors and military air-scouts in photographing mountainous or otherwise inaccessible regions. The physician, surgeon, and dentist rely upon X-ray photographs in the diagnosis of disease. Even the historian uses photographs in reconstructing the past. Instruction and amusement lean heavily upon photography.

Scheele, famous for other brilliant work, discovered the photochemical decomposition of silver chloride in 1777, rightly blaming the darkening on sunlight and proving analytically that the silver chloride is decomposed to silver with loss of chlorine. Daguerre, about 1837, made the great discovery that an invisible image (latent) on silver iodide previously exposed in a camera, could be made visible, or developed, by fuming the plate with mercury vapor. Talbot, about 1839, advanced photography even more than did Daguerre (of "daguerreotype" fame).

The fundamental reaction in photography is that produced by the action of light on the silver halides:



In the dark this reaction is slowly reversed. It is possible that one function of gelatin in sensitive films is to take care of the free chlorine or bromine. Probably a solid solution of silver in silver bromide is formed with release of some bromine. That chlorine is actually set free by the action of light on silver chloride may be shown by the smell. The loss in weight is as much as 8 per cent in a half-year, if the chlorine is allowed to escape. AgCl is not blackened by light if immersed in chlorine water above a certain concentration. The reaction must therefore be reversible. The sensitive film deposited on glass or celluloid is an emulsion (or, more accurately, a suspension) of silver halide in gelatin. There are more silver bromide crystals on a square inch of a photographic plate than there are people on the globe. (See chapter on Colloids.) By means of a lens an image is formed on the plate or film in the camera with varying intensities of light as reflected from white or darker objects. Thus the chemical

effect of light on the silver halide varies throughout the film in accordance with the image. The image is said to be "latent" and is not visible to the eye until a developer (always a reducing solution) completes the reduction of the subhalide to metallic silver. A developer must have sharply selective reducing action, reducing only the exposed silver bromide and not the unexposed. Reduction means the gain of electrons by the silver bromide with release of metallic silver. From the developing bath the plate is taken to a "hypo" bath of sodium thiosulfate, which dissolves any unused silver halide. If this were not washed out, later exposure to the light would render the entire image uniform. The washed and dried negative is then a picture composed of varying thicknesses of metallic silver. This is printed on sensitized paper, which is merely a film much like that of the original plate, backed by paper. Silver chloride papers yield a visible image without further treatment. These are used for "proofs." To make them permanent they are washed with sodium thiosulfate solution to remove unused silver chloride and may then be "toned" in a solution of a gold or a platinum salt. Metallic silver displaces gold from solution, thus converting the image on the paper into the rich red-brown of metallic gold. Platinum prints, prepared in a similar way, are steel gray.

If silver bromide papers are used, a latent image is obtained on printing. It is developed like the original plate. Since bromide papers are extremely sensitive, they are printed by artificial light. Silver halide alone is reduced by a developer but in presence of gelatin only if previously exposed to light.

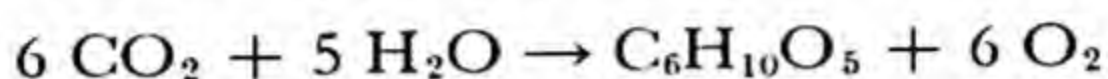
At the beginning of the present century it was hardly possible in astronomy to photograph a spectrum range of more than about 2700 Ångström units, i.e., from 3300 to 6000 Å. But today fully twice that length of spectrum (i.e., from 6000 to 12,000 Å. in the infrared) has been added. Much of this great gain has resulted from the development of better emulsions and sensitizers.

The light energy absorbed by a sensitizing dye may be passed on to the silver halide, possibly increasing the effect in the red and green wave lengths (needed to balance the more active blue and violet wave lengths). Dyes are known that extend the photographic range far into the infrared.

With infrared plates the presence of ammonia was detected in the atmosphere of Jupiter, and carbon dioxide on Venus. Infrared light penetrates atmospheric haze and makes possible photographs of objects 330 miles away, in which the curvature of the earth is clearly visible. It is suggested that since some paints are transparent to infrared light it might be possible to detect corrosion taking place beneath coated surfaces.

Documents made illegible by charring may be read by the aid of infrared photographs. Prisms of LiF, NaCl, and KBr are used in infrared work.

The Photochemistry of Plants. All the vast amount of carbon dioxide thrown into the atmosphere by processes of combustion, of decay, fermentation, and animal respiration is eventually taken up by plants as invaluable food. In the sunlight chlorophyll, the green coloring matter of leaves, is formed and catalyzes the following reaction (probably in stages):



But for this return of oxygen to the air, we should eventually suffer from an oxygen famine and animal life would cease. This $\text{C}_6\text{H}_{10}\text{O}_5$ is starch which may be rearranged into cellulose, the woody fiber of plants. The wonderful laboratory in the green leaf can change starch (insoluble) into soluble sugar for transportation to parts of the plant needing new material. It is there changed again into starch or cellulose.

To use up the carbon dioxide given off by the average man in 24 hours some 60 square meters of green leaf surface are required. Yellow light seems to be most favorable for plant growth. One of the most important problems facing scientists is the discovery of the secret processes by which nature in the green leaf converts radiant energy of the sun into sugars, starches, and cellulose.

Research to find the secret of photosynthesis has recently received powerful aid from compounds containing radioactive carbon as a tracer element.

Ultra-violet Light. Light waves from the sun extend into the ultra-violet region to about $290 \text{ m}\mu$, all shorter being absorbed in passing through our atmosphere. The rays from this limit of $290 \text{ m}\mu$ to about $310 \text{ m}\mu$ have been shown to be very beneficial in the cure of rickets, surgical tuberculosis, in hastening the cure of wounds, and in improving the general health and growth of those receiving such radiations.

Ordinary glass transmits a portion of the ultra-violet nearest the visible region of the spectrum, but entirely eliminates vital rays between $290 \text{ m}\mu$ and $310 \text{ m}\mu$. Quartz glass is very transparent to such waves but is extremely expensive.

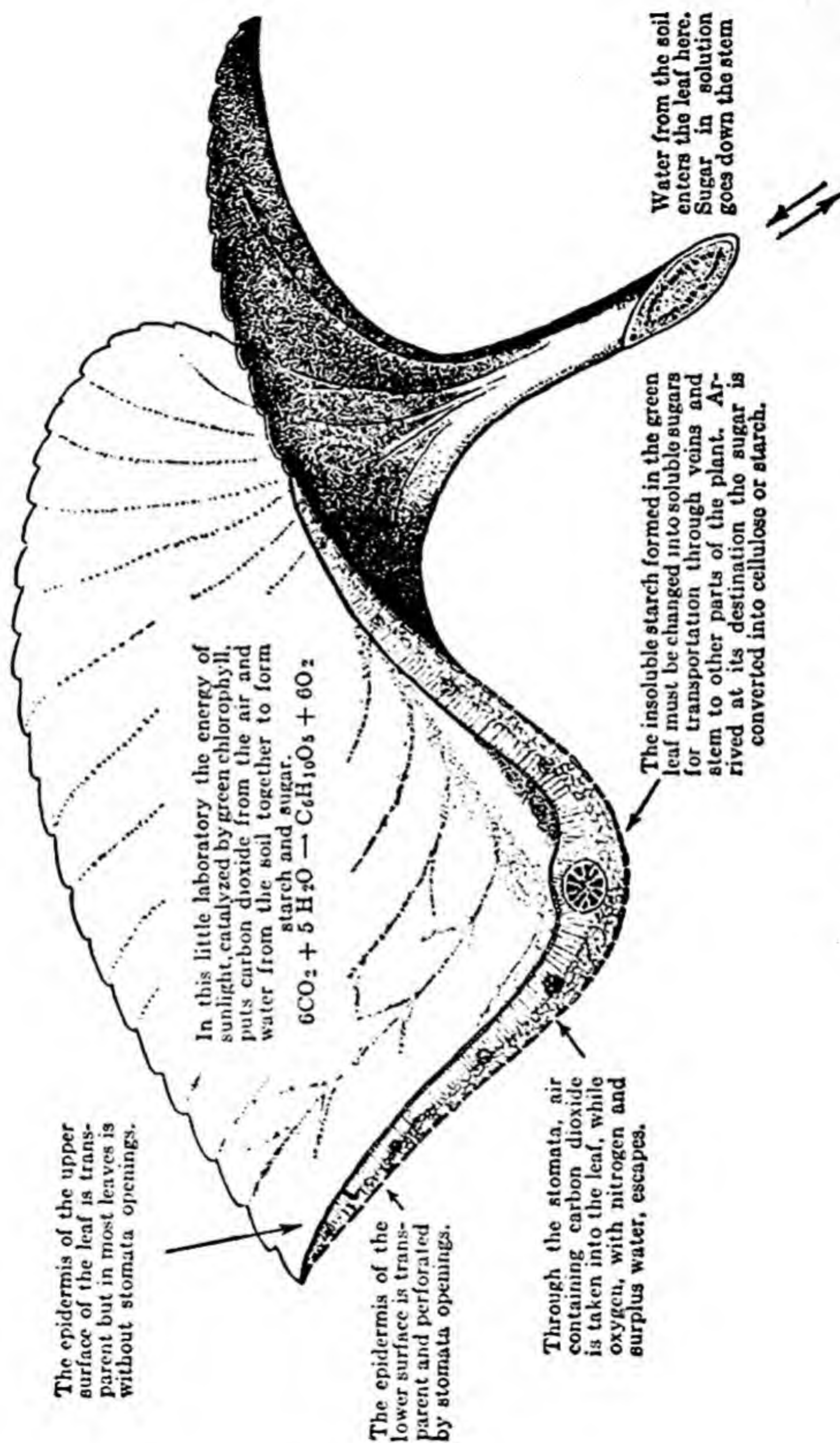


Fig. 182. The green leaf laboratory.

Huge synthetic crystals are now serving science in regions of the ultra-violet and infrared where glass has unfortunate limitations. A prism of rock salt transmits out to 200,000 Ångströms in wave length. Lithium fluoride transmits far out in the ultra-violet region.

Sterilizing lamps are now used in operating rooms of hospitals and in rooms for cold storage of foods. With their aid in killing molds that would develop at a temperature suitable for rapid

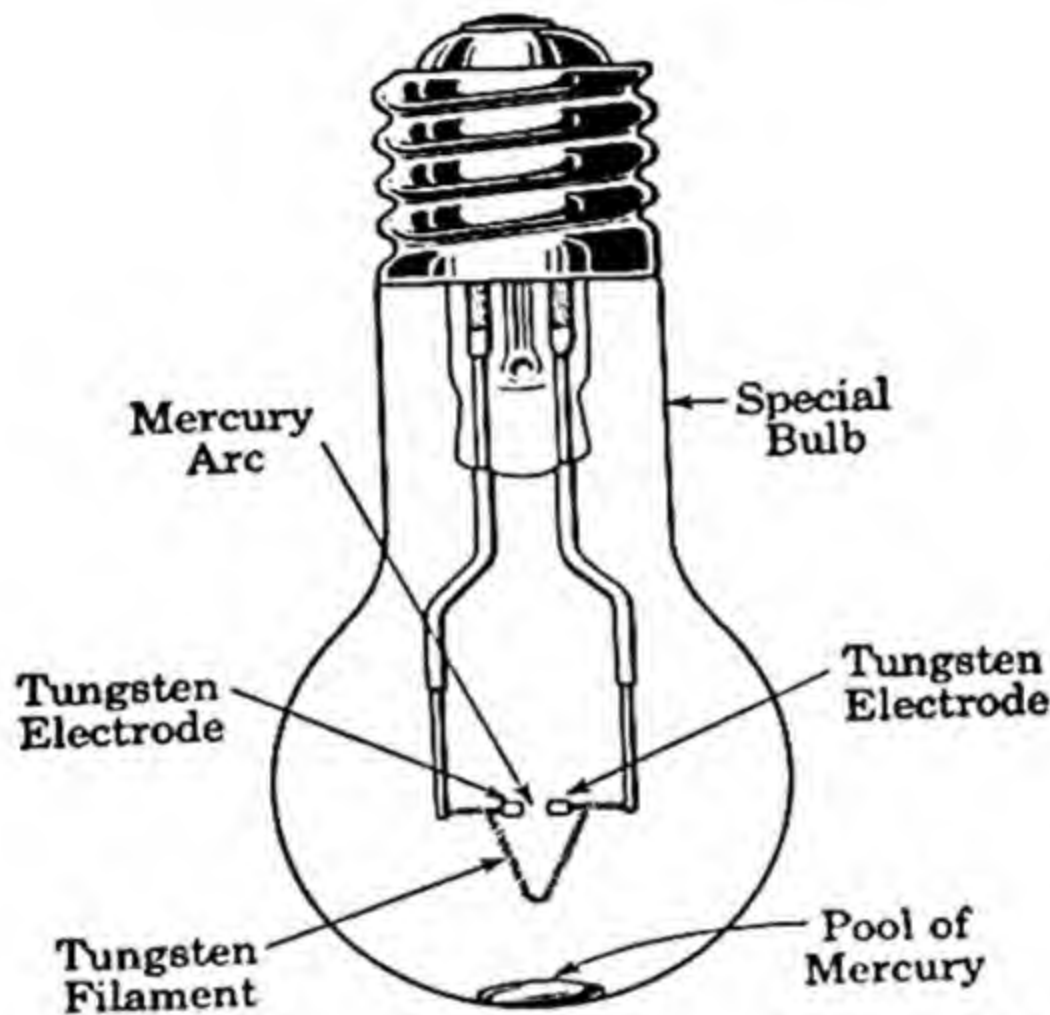


Fig. 183. The "Sunlight Lamp." Heat from the tungsten filament volatilizes a little mercury and there results a mercury arc, rich in healing, ultra-violet rays. The special glass of the bulb permits passage of just enough ultra-violet to give a light bath at three feet equal in medical effect to midsummer at noon. (General Electric Co.)

tenderizing of beef by enzymes present, tough meat may be made more valuable. For killing bacteria the most effective ultra-violet wave length seems to be 2537 Å.

A few commercial glasses with very good ultra-violet transmission have been developed recently for sun rooms and hospitals.

Thin films of powdered silver and gold are transparent to ultra-violet light but opaque to the visible. Naturally ultra-violet photographs must be taken with a quartz or transmitting glass lens properly silvered.

The sun's ultra-violet light, especially shorter wave lengths that are cut off by the miles of air in our atmosphere, converts the dry upper oxygen into ozone, and perhaps ionizes some of the air, forming a downward-reflecting ceiling for radio waves.

Infrared rays are too long to be seen, and too short to be heard in radio receivers but they can be measured as heat by a bolometer — a device in which the electrical conductivity is altered by heat rays.

The latest and most sensitive is the Andrews bolometer in which a strip of columbium nitride, when cooled to near absolute zero becomes "superconductive." When warmed only one millionth of a degree the bolometer gives a clear electrical signal. It can register heat waves from the body of a man 500 yards distant.

The "sniperscope," an infrared telescope mounted on a carbine, enables a soldier in total darkness to hit a target the size of a man at 75 yards. The similar "snooperscope" attached to a driver's helmet has enabled scout cars to speed over roads at 50 miles an hour without lights. The infrared rays or black light from objects make a visible image on a suitable screen. Infrared filters on searchlights make it possible to throw beams of this invisible light on enemy tanks at night, and the rays are reflected back and made visible.

Fluorescence. Fluorescence on radiation by strong ultra-violet light (in the dark) is an important analytical tool. Cellulose acetate fluoresces strongly while cellulose nitrate fluoresces but little. Many substances can be identified in this way. Quinine shows fluorescence in acid but not in alkaline solution and so could be used as an indicator.

Now fluorescent lamps are in common use. The ultra-violet rays from mercury vapor in the tube excite certain fluorescent substances lining the lamp. White light or colored may be produced with superior efficiency.

The fluorescent lamp is three times as efficient, in terms of light for current used, as the tungsten filament lamp.

Electrons in vacuum tubes are driven from the cathode in three ways: high voltage, heating, and light. In fluorescent lighting tubes the cathode is sometimes coated with barium oxide or strontium oxide because these substances emit electrons more readily than the metal cathode beneath.

"Phosphors" is a term used to designate substances that fluoresce in ultra-violet light or other radiation. Zinc silicate mineral fluoresces with a yellow light under X-ray treatment. It may be activated by a little manganese impurity, and made to fluoresce better. So activated, it is best excited by ultra-violet at 2537 Å. Zinc sulfide phosphor is at its best in the near ultra-violet. Although zinc sulfide prepared by heating thirty minutes at 900° will fluoresce light blue, the presence of 10^{-5} fraction of cupric sulfide in the mixture will change the fluorescence to a brilliant green.

The rapid commercial development of fluorescent lamps has forced superrefinements in preparation of the fluorescent coatings due to the fact that traces of certain impurities such as iron may decrease fluorescence to nearly nothing. Television tubes are coated with phosphors.

Chemiluminescence. Most chemiluminescent reactions are oxidations. The most striking of these is the oxidation of 3-aminophthalhydrazide ("luminol") by hydrogen peroxide and potassium ferricyanide in dilute alkaline solution. The beauty of the light is astonishing, and it lasts several minutes.

Making the solution slightly acid, with dilute sulfuric, stops the luminescent reaction but upon further addition of alkali (NaOH) the light is again radiated beautifully — and without apparent heat. "Luminol" can be purchased from the Eastman Kodak Company or prepared as directed in *J. Chem. Ed.*, 11, 142 (1934).

Light produced by living organisms is due to two separable substances, luciferin which is oxidized in air and moisture, and luciferase. When the two are mixed light is radiated.

The Photoelectric Cell. "Metals differ in power of emitting electrons under illumination. Best conditions are obtained by putting the metal in a glass or quartz enclosure, and controlling both the kind of atmosphere and its pressure. The more electro-positive the metal, the more photo-sensitive; so in place of zinc and copper, in the earlier studies, an alkali metal, potassium, rubidium, or cesium, is used in non-reacting atmospheres — an

inert gas, argon, helium, or neon — at a low pressure suitable for multiplying the photo-current by the electric conduction induced in the gas by collision of the electrons with the gas atoms.

“The typical photoelectric cell is a glass bulb, with one electrode, the cathode, usually a layer of alkali metal on the inner surface, with a wire leading out through the glass, and another electrode, the anode, a loop of wire, likewise carried out. Connect these two wires through a galvanometer and let light shine into the bulb; the galvanometer will show an electric current flowing. The current starts and stops instantaneously; it is proportional to the illumination. It is quite small, but with proper instruments it may be used to measure the intensity of light from such faint objects as sixth magnitude stars.” (Herbert E. Ives.)

With an outside electromotive force, as from a battery, these electrons — or *photoelectrons* as they are termed when driven out of atoms by radiations — will carry the current.

The alkali metals are most favored as the light-sensitive material of photoelectric cells and of these cesium is the best — at \$4000 per pound!

The photoelectric cell is at its best when the bulb is filled with argon at 0.1 mm.

For the talking pictures a beam of light passing through the sound tracks on the film hits a photoelectric cell with variations in light intensity which are reproduced through the amplifier and loud speaker as sound and speech.

Since the photoelectric cell can (upon interruption of a beam of light between cell and mirror) cause relay contacts to close, it is possible by its aid to operate signals, power switches, counters of people and moving objects, or to start and stop machines, close elevator doors, and turn lights on and off.

The Spectroscope. A beam of sunlight passing through a transparent prism is dispersed into the colors composing white light (Fig. 184). This is due to the fact that in entering one transparent medium from another the different wave lengths of light are bent in different degrees. Against a white screen these colors are projected in a band called the spectrum. The spectroscope (Fig. 185) consists of a glass prism, a tube containing lenses and

an adjustable slit to admit a narrow beam of light, a telescope with which to view the spectrum, and a third tube which pro-

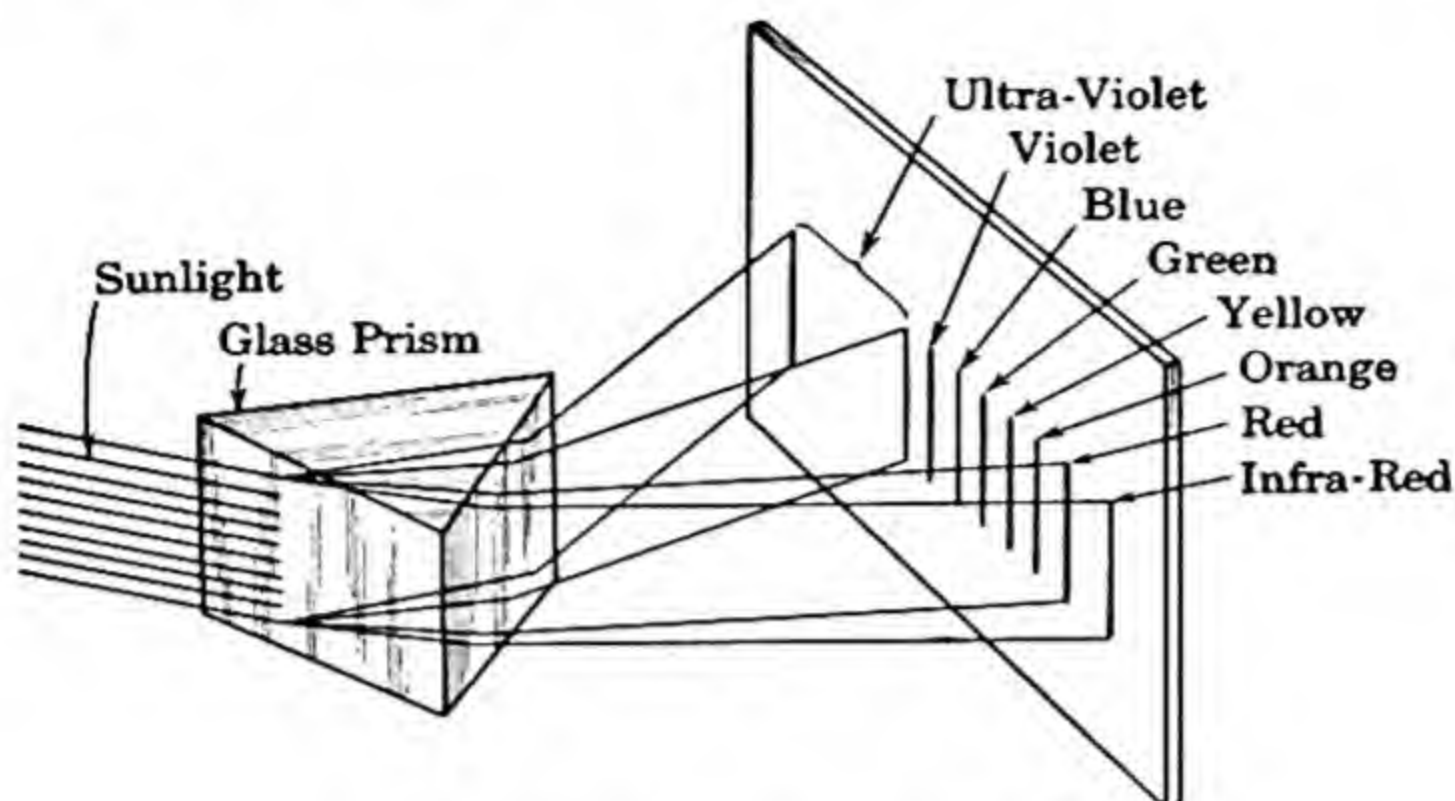


Fig. 184. The solar spectrum.

jects the image of a measuring scale on the field. Small direct-vision spectroscopes are made of a single tube with lens, prism, and slit inside the tube.

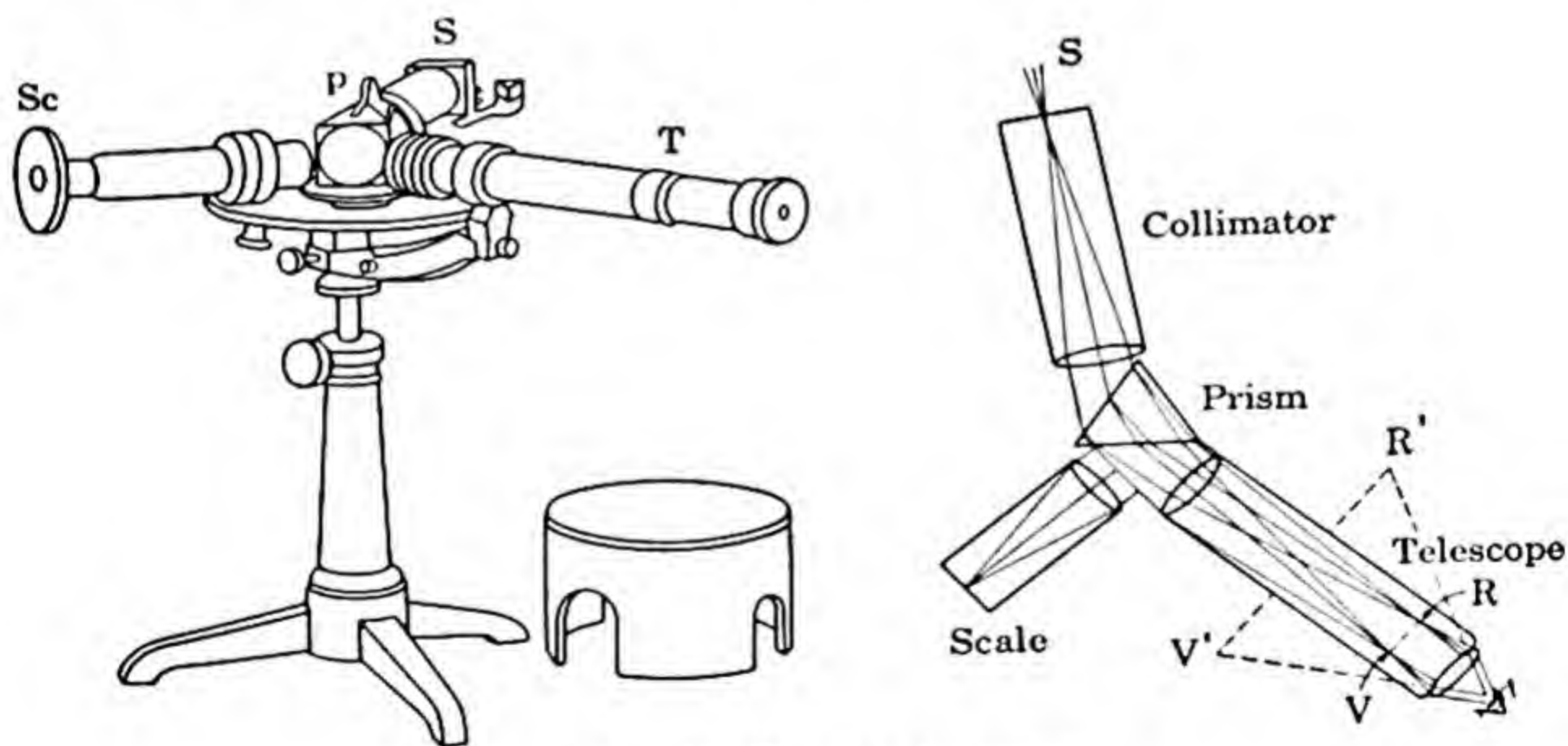


Fig. 185. The spectroscope.

Bright-line Spectra. An incandescent solid gives a continuous spectrum of all wave lengths. An incandescent gas gives a spectrum made up of one or more bright lines, sometimes a large

number. These are always characteristic of each element, both in color and in the exact position of the lines. For example, if light from a sodium flame is viewed through the spectroscope, a single yellow line is observed. Incandescent helium gives a spectrum of definitely located red, yellow, green, and blue lines, and may be recognized by them.

Electrons move in definite orbits or levels related to their energy and yet there must be sub-levels to account for all the spectral lines.

Bunsen and Kirchhoff, in 1860, working with the spectroscope which they had just invented, discovered certain peculiar bright lines in the spectrum of the residue from a spring water. This clue led them to the discovery of the element cesium, responsible for the lines. Rubidium (discovered the next year in lepidolite) receives its name from two very bright red lines, and cesium (*cæsius*, sky-blue) from two bright blue lines. Compounds of these elements are found in very small amounts in carnallite and in lepidolite.

Dark-line Spectra. The spectrum of the incandescent sun is really not continuous but contains many dark lines (Frauenhofer lines, because they were first mapped by Frauenhofer in 1814).

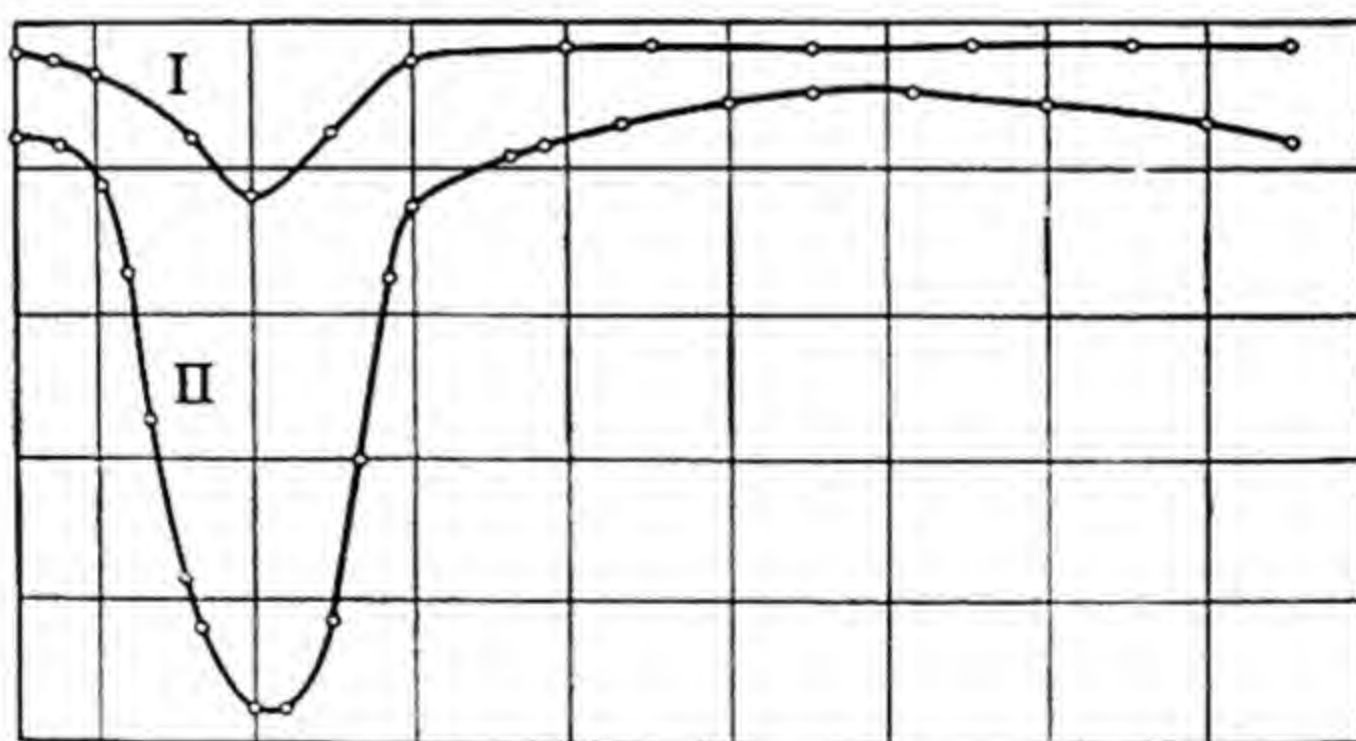
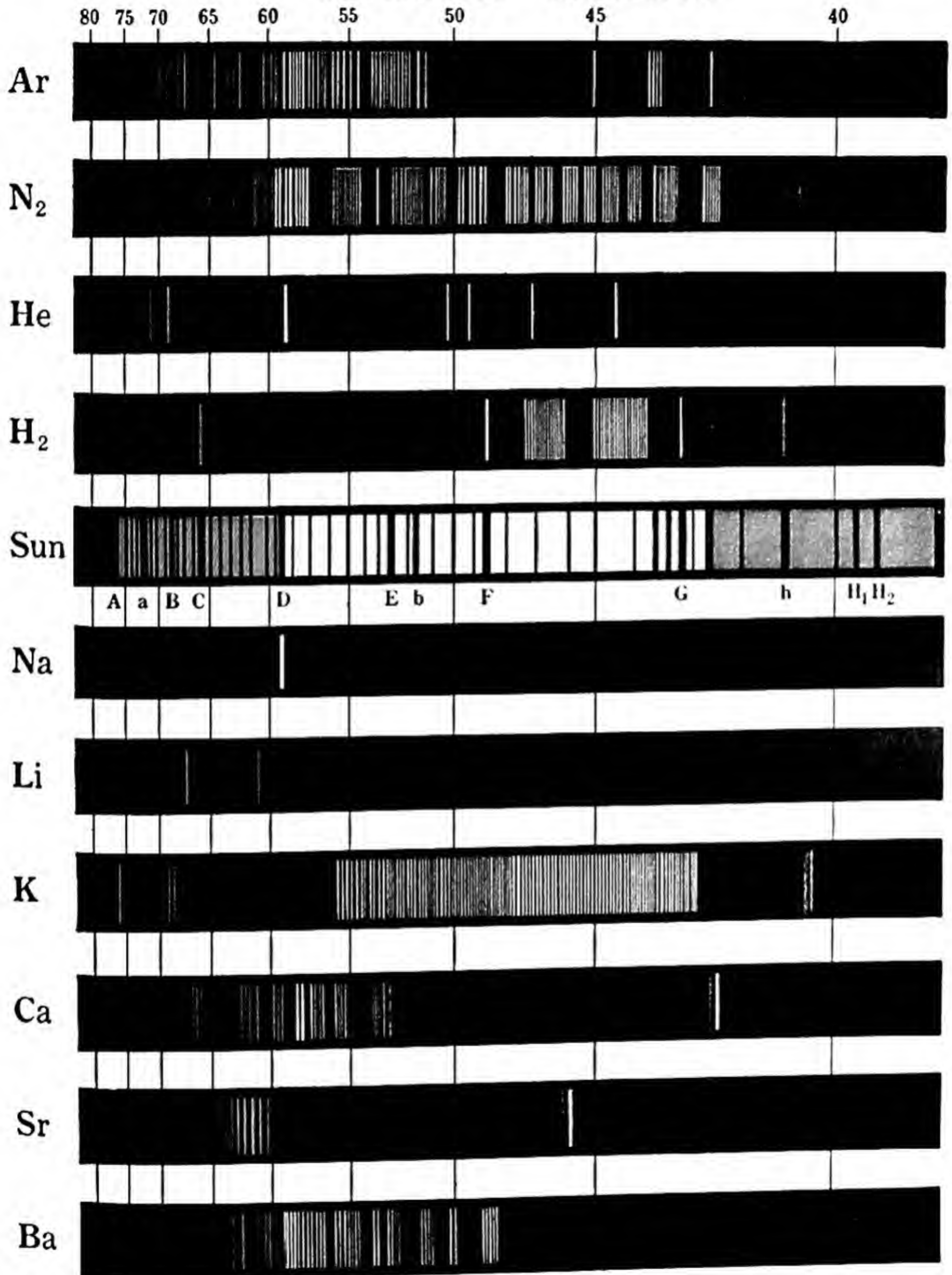


Fig. 186. The absorption of light of a definite wave length may be characteristic of a substance. In the spectrogram above curve I represents light transmission (and absorption) of 1 gram of cobalt sulfate per liter of aqueous solution. Curve II represents the proportionately greater absorption by a solution of ten times this concentration.

These are explained by the fact that when, for example, light from a white-hot solid passes through a yellow sodium flame there is a dark line in the yellow part of the spectrum. In other

PLATE OF SPECTRA



From *Inorganic Chemistry*, by H. P. Cady.
By permission of the author and McGraw-Hill Book Co., Publishers

5. What were the military uses of infrared rays?
6. Could absorption spectra help identify human blood?
7. How do plants utilize the carbon dioxide of air?
8. What is the chemistry of photography?
9. How does an excited atom radiate light?
10. Of what commercial use are "phosphors"?

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APPENDIX

VITAL STRATEGIC MATERIALS, NOT ADEQUATELY PRODUCED IN THE UNITED STATES

MATERIAL		CHIEF SOURCE	CHIEF USES
Rubber (natural)	°	East Indies	Tires, etc.
Tin	°	East Indies	Bronze, bearings, tin-plating
Quinine	°	East Indies	Antimalarial
Antimony	*	China	Type metal
Silk	°	Japan	Clothing, powder bags, parachutes
Coconut oil	°	The tropics	Soap
Tung oil	*	China	Varnishes, paints, lithograph inks
Linseed oil	**	Argentina	Paints and varnishes
Industrial diamonds	°	Brazil and South Africa	Cutting and grinding
Quartz crystals	*	Brazil	Radio and radar
Coffee	°	Brazil	Morale builder
Nickel	°	Canada	Stainless steel
Manganese	*	Brazil	Steel
Tungsten	**	China	Steel (high-speed tools)
Vanadium	***	Peru	Steel
Hides	**	Argentina	Leather
Wool	**	Argentina and Australia	Clothing
Jute	°	India	Burlap
Mica	*	India	Electrical insulation
Chromium, soon to be inde- pendent		New Caledonia, Turkey, Cuba, South Africa, India, Russia	Stainless steel, etc.
Platinum	*	Canada	Catalyst, scientific apparatus
Bauxite for aluminum		South America	Light metal

The sign ° means little or no production, *, small production, **, large production, ***, very large production.

It is true that our production of such necessary materials as copper, zinc, lead, paper, alcohol, and gasoline is enormous, yet the demands of World War II forced rationing of these items. It is predicted that our copper, lead and zinc ores will be exhausted in a life time.

*Marks substances used in manufacture or operation of items below.						Copy this chart and extend this part.					
		NaOH	NH ₃	CH ₃ OH	Cellulose etc.						
Aircraft											
Aluminum											
Cleansers											
Explosives		*									
Glass											
Iron and Steel											
Laundries											
Leather											
Machine Tools											
Paint and Varnish											
Paper				*							
Plastics											
Rayon	*										
Refrigerators											
Rubber											
Soap											
Storage Batteries											

Sugar is also necessary, and we produce only 1,000,000 tons yearly from beets, but we can get the remaining 6,000,000 tons from near-by Cuba and Puerto Rico.

Necessity stimulated the invention of substitutes for some of these materials, e.g., synthetic rubber for the natural product, yet it is obvious that great stock piles of most of them should be maintained for national defense and as insurance against unfair price increases by foreign monopolies.

HYDROGEN-ION CONCENTRATIONS EXPRESSED IN pH VALUES

The pH Notation.¹ It is now the custom among biologists and many chemists to express degrees of acidity and alkalinity in pH values instead of normalities. By the pH value is meant the logarithm of the number of liters of a solution which must be taken in order to contain

¹ Adapted from a pamphlet by W. A. Taylor of the La Motte Chemical Products Company.

1 gram-ion of hydrogen (1.008 g. of H^+). There is only 1 gram-ion of hydrogen in 10,000,000 liters of pure water for water is only minutely ionized. Since the log of 10,000,000 is 7 it is evident the pH value of pure water, or of a neutral solution, is 7.

The pH values below 7.0, such as 6.0, 5.0, etc., denote acidity, the degree of acidity increasing as the numbers decrease. For example, if a small amount of HCl is added to pure distilled water which has an H-ion concentration of 10^{-7} or a pH value of 7.0, the acid will dissociate into positive H ions and negative Cl ions. The total number of H ions in the solution will, therefore, be greater than 10^{-7} , and the solution will therefore be acid. Suppose the H-ion concentration is found to be

$\frac{N}{1,000,000}$; in other words, 1,000,000 liters contain 1 gram ion of hydrogen. The pH value will be the log of 1,000,000, which is 6.0.

Similarly, if the H-ion concentration is $\frac{N}{100,000}$, the pH value will be

5.0, etc. It should be remembered that, since we are dealing with logarithmic values, a solution having a pH value of 6.0 contains 10 times as many H ions as one having a pH value of 7.0. Similarly, a solution of pH 5.0 contains 100 times as many H ions as one of pH 7.0.

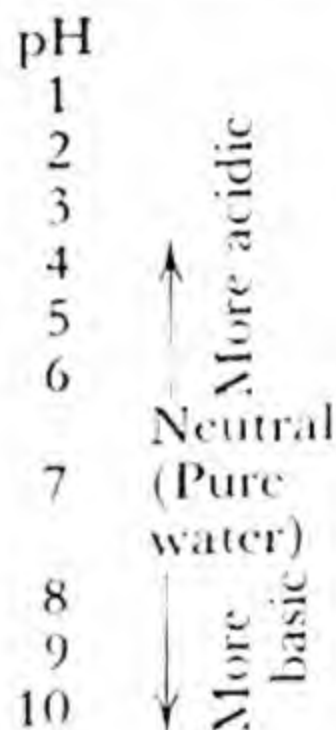
The pH scale indicates a measure of the actual or effective concentration of H^+ ions present in the solution while normality indicates the grand total of actual and potential ions.

Equal volumes of 0.1 N hydrochloric acid and 0.1 N acetic acid contain the same number of grams of actual plus potential H^+ ions, yet the pH value of 0.1 N hydrochloric acid is 1.0 and of 0.1 N acetic acid 2.9. This is simply a reminder that the number of H^+ ions actually present and effective is greater with the strong hydrochloric acid than with the weak acetic acid.

An N/10 solution of acetic acid contains 0.1 g of *ionizable* H per liter. Electrical conductivity measurements show, however, that at 18° C. it is dissociated only to the extent of 1.36%. Hence the hydrogen-ion concentration is $0.1 \times 0.0136 = 0.00136$ g. per liter. This is equivalent to an N/735 solution of H ions. The pH value of N/10 acetic acid is therefore the log of 735, which is 2.86

Since by the law of mass action

$$\text{Conc. of H Ions} \times \text{Conc. of OH Ions} = \text{a Constant}$$



it is apparent that as the H-ion concentration increases the OH-ion concentration must decrease, and vice versa. *Even in a strongly alkaline solution* there are, however, some H ions and, for the sake of simplicity, it is advisable to express both acidity and alkalinity in terms of pH values.

These pH values may be determined by the Hydrogen Electrode or by use of a series of special indicators. In the following table Clark and Lubs show how to follow the range of pH values by trial with various indicators.

COMMON NAME	COLOR CHANGE ACID-ALKALINE	pH RANGE
Thymol blue (acid range)	Red-yellow	1.2-2.8
Brom phenol blue	Yellow-red	3.0-4.6
Methyl red	Red-yellow	4.4-6.0
Brom cresol purple	Yellow-purple	5.2-6.8
Brom thymol blue	Yellow-blue	6.0-7.6
Phenol red	Yellow-red	6.8-8.4
Cresol red	Yellow-red	7.2-8.8
Thymol blue (alkaline range)	Yellow-blue	8.0-9.6
Cresol phthalein	Colorless-red	8.2-9.8

[H ⁺]	10 ⁰	10 ⁻¹	10 ⁻²	10 ⁻³	10 ⁻⁴	10 ⁻⁵	10 ⁻⁶	10 ⁻⁷	10 ⁻⁸	10 ⁻⁹	10 ⁻¹⁰	10 ⁻¹¹	10 ⁻¹²	10 ⁻¹³	10 ⁻¹⁴
pH	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14
pOH	14	13	12	11	10	9	8	7	6	5	4	3	2	1	0
[OH ⁻]	10 ⁻¹⁴	10 ⁻¹³	10 ⁻¹²	10 ⁻¹¹	10 ⁻¹⁰	10 ⁻⁹	10 ⁻⁸	10 ⁻⁷	10 ⁻⁶	10 ⁻⁵	10 ⁻⁴	10 ⁻³	10 ⁻²	10 ⁻¹	10 ⁰
Strong Acid			Neutral Solution						Strong Base						

Fig. 187.

Buffered Solutions. Mixtures of weak acids and their salts or of weak bases and their salts are called buffered solutions because they are protected against change in hydrogen-ion concentration when small amounts of acids or bases are added. Dilution changes the pH of buffered solutions very little.

Acid solutions are buffered by addition of salts of weak acids, sodium acetate, for example, while basic solutions are buffered by salts of weak bases such as ammonium chloride. Blood and fruit juices are buffered in their natural state.

In the blood carbonic acid is buffered by NaHCO₃, Na₂HPO₄, and NaH₂PO₄ so that the pH is held very closely to 7.4. If it drops below 6.95 or rises above 7.7 death may result.

pH VALUES OF SOME FOODS

Apples	2.9-3.3	Milk, cows	6.3-6.6
Cabbage	5.2-5.4	Potatoes	5.6-6.0
Cherries	3.2-4.0	Spinach	5.1-5.7
Lemons	2.2-2.4	Strawberries	3.0-3.5
Oranges	3.0-4.0	Pure water	7.00-7.00

SOLUBILITY PRODUCTS AT 20°

The solubility product is the equilibrium constant for the saturated solution of a solid strong electrolyte (slightly soluble).

ELECTROLYTE	K	ELECTROLYTE	K
HgCl	2×10^{-18}	Fe(OH) ₂	1.64×10^{-14}
AgCl	1.56×10^{-10}	Fe(OH) ₃	1.1×10^{-36}
AgBr	4×10^{-13}	Mg(OH) ₂	1.2×10^{-11}
AgI	1.5×10^{-16}	Mn(OH) ₂	4×10^{-14}
		Al(OH) ₃	3.7×10^{-15}
AgOH	1.5×10^{-8}		
BaCO ₃	7×10^{-9}	CuS	8.5×10^{-45}
CaCO ₃	0.87×10^{-9}	CdS	3.6×10^{-29}
SrCO ₃	1.6×10^{-9}	FeS	3.7×10^{-19}
CaSO ₄	6.1×10^{-6}	NiS	1.4×10^{-24}
BaSO ₄	0.87×10^{-10}	ZnS	1.2×10^{-23}
SrSO ₄	2.8×10^{-7}	HgS	3×10^{-53}
PbCrO ₄	3.3×10^{-14}	PbC ₂ O ₄ (oxalate)	2.74×10^{-11}
CaC ₂ O ₄	2.57×10^{-9}	PbS	3.4×10^{-28}

PRESSURE (OR TENSION) OF WATER VAPOR IN
MILLIMETERS OF MERCURY

TEMPERATURE	PRESSURE	TEMPERATURE	PRESSURE
0°	4.6	21°	18.7
5°	6.5	22°	19.8
10°	9.2	23°	21.0
12°	10.5	24°	22.4
15°	12.8	25°	23.8
16°	13.6	26°	25.2
17°	14.5	27°	26.7
18°	15.5	28°	28.3
19°	16.5	29°	30.
20°	17.6	30°	31.8

SPECIFIC GRAVITY OF METALS

Osmium	22.48	Chromium	7.1
Platinum	21.45	Tin	7.1
Gold	19.32	Zinc	7.5
Tungsten	19.3	Aluminum	2.70
Vanadium	5.96	Beryllium	1.84
Mercury	13.55	Magnesium	1.74
Lead	11.34	Calcium	1.55
Silver	10.5	Sodium	0.97
Copper	8.93	Potassium	0.97
Iron	7.86		

MELTING POINTS OF METALS AND A FEW NON-METALS

Mercury	-38.87° C.	Silver	960.5° C.
Cesium	+28.3°	Gold	1063.0°
Gallium	30°	Copper	1083.0°
Rubidium	38.5°	Manganese	1260.0°
Phosphorus	44.10°	Beryllium	1300°
Potassium	63°	Silicon	1420.0°
Sodium	97.7°	Nickel	1452.0°
Sulfur (rhombic)	112.8°	Cobalt	1480.0°
Sulfur (monoclinic)	119.0°	Iron	1535.0°
Iodine	114°	Chromium	1615.0°
Lithium	186.0°	Vanadium	1710.0°
Selenium	220.0°	Platinum	1755.0°
Tin	231.85°	Uranium	1850.0°
Bismuth	271.3°	Rhodium	1955.0°
Cadmium	320.9°	Boron	2300.0°
Lead	327.5°	Iridium	2350.0°
Zinc	419.4°	Molybdenum	2620°
Tellurium	452.0°	Osmium	2700.0°
Antimony	630.5°	Tantalum	3000°
Magnesium	651.0°	Tungsten	3370.0°
Aluminum	660.0°	Carbon (graphite)	3700.0°
Calcium	810.0°		
Barium	850.0°		
Radium	960.0°		

WEIGHT IN GRAMS OF 1 LITER OF VARIOUS GASES

(Standard Conditions)

Air	1.2929	Hydrogen chloride	1.6392
Ammonia	0.7710	Hydrogen sulfide	1.5390
Argon	1.7832	Methane	0.7168
Carbon dioxide ^a	1.9769	Nitric oxide	1.3402
Carbon monoxide	1.2504	Nitrogen	1.2505
Chlorine	3.2140	Nitrous oxide	1.9778
Helium	0.1785	Oxygen	1.4290
Hydrogen	0.0898	Sulfur dioxide	2.9269

^a The density of CO₂ referred to air is $\frac{1.9769}{1.2929} = 1.53$.

THE ELECTRICAL CONDUCTIVITY OF METALS

(International Annealed Copper Standard - 100)

MATERIAL	VOLUME CONDUCTIVITY	MASS CONDUCTIVITY
Silver	105.	88.2
Copper	100.	100.0
Aluminum	61.	200.7
Magnesium	38.6	197.2
Zinc	29.7	37.2
Brass	24.6	25.5
Nickel	22.1	22.1
Tin	15.0	18.3
Lead	7.8	6.1

The values marked "volume conductivity" compare the electrical conductivities of equal lengths of wire of the same diameter. The values marked "mass conductivity" compare the electrical conductivities of pieces of wire of the same *length* and *weight*; of course, the diameters will vary inversely as the densities. Copper is given an arbitrary value of 100 in each case. Note that, weight for weight, aluminum has a higher conductivity than the other metals and alloys.

STANDARD UNITS OF MEASURE

The centimeter is 0.01 of the distance between two marks on a standard meter bar kept at the International Bureau of Weights and Measures.

The liter is the volume of 1 kilogram of water at maximum density.

$$1 \text{ liter} = 1000.027 \text{ cubic centimeters} = 1000 \text{ milliliters}$$

The gram is 0.001 of a standard mass of 1 kilogram weight kept at the International Bureau of Weights and Measures.

$$1 \text{ micron} = 10^{-3} \text{ mm. } (= 1 \mu)$$

$$1 \text{ millimicron} = 10^{-6} \text{ mm. } (= 1 \text{ m}\mu)$$

There is a growing tendency to use 1 ml. (0.001 liter) as slightly more exact than 1 cc.

CONVERSION TABLE

Metric and English Systems

1000 millimeters (mm.) = 1 meter	2.54 cm.	= 1 inch
100 centimeters (cm.) = 1 meter	1 meter	= 39.37 inches
10 millimeters = 1 cm.	1 liter	= 1.06 quarts
	1 gram	= 15.4 grains
1000 grams = 1 kilogram (kg.)	1 kilo	= 2.20 pounds
1000 milliliter = 1 liter	28.35 grams	= 1 ounce av.
1 cu. ft. = 28.32 liters	1 pint	= 16 fluid oz.
1 lb. av. = 453.59 g.	1 teaspoon	= 4 cc.
1 oz. av. = 28.35 g.	1 gallon (U. S.)	= 3785.4 ml.
1 liter = 1.0567 liquid quarts (United States)	1 gram	
1 gallon = 3.7853 liters	(15.4 + grains) = 0.0353 oz.	
	28.3495 gram = 1 oz.	
1 cm. = 0.3937 in.	1 kilogram	= 2.2046 lb.
2.54 cm. = 1 in.	0.4536 kilogram	= 1 lb.
1 meter = 3.28 ft.	1 drop of water	= 1/20 ml.
0.3048 meter = 1 ft.	1 teaspoonful	= 4 ml.
	1 tablespoonful	= 16 ml.
1 kilometer = 0.6214 mi.	1 fluid ounce	= 29.57 ml.
1.6093 kilometer = 1 mi.	1 cup	= 240 ml.

Note that 1 cc. and 1 ml. are almost identical.

The metric system is essentially a decimal system, making calculations easier. As it is now, we in America are not consistent, for we use a decimal system of money, while machine-shop practice deals with a thousandth of an inch as well as the half, quarter, eighth, etc.

It is interesting to note that the meter is about 10 per cent longer than the yard, the half-kilo (world pound) about 10 per cent heavier

than the common pound, and the liter about 5 per cent larger than the quart.

A dime is about 1 mm. thick and weighs 2.5 grams.

TABLE OF STABLE ISOTOPES (1944)

In Order of Decreasing Abundance for Each Element (Fractions Disregarded)

ATOMIC NUMBER	ELE- MENT	MASS OF ISOTOPES	ATOMIC NUMBER	ELE- MENT	MASS OF ISOTOPES
1	H	1, 2	38	Sr	88, 86, 87, 84
2	He	4	39	Y	89
3	Li	7, 6	40	Zr	90, 92, 94, 91, 96
4	Be	9	41	Cb	93
5	B	11, 10	42	Mo	98, 96, 95, 92, 97, 94, 100
6	C	12, 13	43	Te	(?)
7	N	14, 15	44	Ru	102, 104, 101, 99, 100, 96, 98
8	O	16, 18, 17	45	Rh	103
9	F	19	46	Pd	108, 106, 105, 110, 104, 102
10	Ne	20, 22, 21	47	Ag	107, 109
11	Na	23	48	Cd	114, 112, 111, 110, 113, 116, 106, 108
12	Mg	24, 25, 26	49	In	115, 113
13	Al	27	50	Sn	120, 118, 116, 119, 117, 124, 122, 112, 114, 115
14	Si	28, 29, 30	51	Sb	121, 123
15	P	31	52	Te	130, 128, 126, 125, 124, 122, 123, 120
16	S	32, 34, 33, 36	53	I	127
17	Cl	35, 37	54	Xe	132, 129, 131, 134, 136, 130, 128, 124, 126
18	A	40, 36, 38	55	Cs	133
19	K	39, 41, 40	56	Ba	138, 137, 136, 135, 134, 130, 132
20	Ca	40, 44, 42, 43, 48, 46	57	La	139
21	Sc	45	58	Ce	140, 142, 136, 138
22	Ti	48, 46, 47, 49, 50	59	Pr	141
23	V	51	60	Nd	142, 144, 146, 143, 145, 148, 150
24	Cr	52, 53, 50, 54	61	Pm	(?)
25	Mn	55	62	Sm	152, 154, 147, 149, 148, 150, 144
26	Fe	56, 54, 57, 58			
27	Co	59			
28	Ni	58, 60, 62, 61, 64			
29	Cu	63, 65			
30	Zn	64, 66, 68, 67, 70			
31	Ga	69, 71			
32	Ge	74, 72, 70, 73, 76			
33	As	75			
34	Se	80, 78, 76, 82, 77, 74			
35	Br	79, 81			
36	Kr	84, 86, 82, 83, 80, 78			
37	Rb	85, 87			

ATOMIC NUMBER	ELE- MENT	MASS OF ISOTOPES	ATOMIC NUMBER	ELE- MENT	MASS OF ISOTOPES
63	Eu	153, 151	78	Pt	195, 194, 196, 198, 192
64	Gd	158, 160, 156, 157, 155, 154, 152	79	Au	197
65	Tb	159	80	Hg	202, 200, 199, 201, 198, 204, 196
66	Dy	164, 163, 162, 161, 160, 158	81	Tl	205, 203
67	Ho	165	82	Pb	208, 206, 207, 204
68	Er	166, 168, 167, 170, 164, 162	83	Bi	209
69	Tm	169	84	Po	(?)
70	Yb	174, 172, 173, 176, 171, 170, 168	85	At	(?)
71	Lu	175, 176	86	Rn	(?)
72	Hf	180, 178, 177, 179, 176, 174	87	Fr	(?)
73	Ta	181	88	Ra	226, 228, 280, 232 unstable
74	W	184, 186, 182, 183, 180	89	Ac	(?)
75	Re	187, 185	90	Th	232(?)
76	Os	192, 190, 189, 188, 187, 186, 184	91	Pa	231(?)
77	Ir	193, 191	92	U	238, 235, 234, 233
			93	Np	237
			94	Pu	239
			95	Am	241 (500 yrs.)
			96	Cm	242 (150 days)

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